A COMPARISON OF MODELING APPROACHES IN SIMULATING CHLORINATED ETHENE REMOVAL IN A CONSTRUCTED WETLAND BY A MICROBIAL CONSORTIA

THESIS

Jason S. Campbell, Captain, USAF

AFIT/GEE/ENV/02M-02

DEPARTMENT OF THE AIR FORCE
AIR UNIVERSITY
AIR FORCE INSTITUTE OF TECHNOLOGY

Wright-Patterson Air Force Base, Ohio

The views expressed in this thesis are those of the author and do not reflect the official policy or position of the United States Air Force, Department of Defense, or the U.S. Government.

AFIT/GEE/ENV/02M-02

A COMPARISON OF MODELING APPROACHES IN SIMULATING CHLORINATED ETHENE REMOVAL IN A CONSTRUCTED WETLAND BY A MICROBIAL CONSORTIA

THESIS

Presented to the Faculty

Department of Systems and Engineering Management

Graduate School of Engineering and Management

Air Force Institute of Technology

Air University

Air Education and Training Command

In Partial Fulfillment of the Requirements for the

Degree of Master of Science in Engineering and Environmental Management

Jason S. Campbell, BS

Captain, USAF

March 2002

AFIT/GEE/ENV/02M-02

A COMPARISON OF MODELING APPROACHES IN SIMULATING CHLORINATED ETHENE REMOVAL IN A CONSTRUCTED WETLAND BY A MICROBIAL CONSORTIA

Jason S. Campbell, BS
Captain, USAF

Approved:

Michael L. Shelley (Chairman)	8 Mar 02 date
James P. Amon (Member)	28 Feb 02 date
Charles A. Bleckmann (Member)	11 March 02 date
Mark N. Goltz (Member)	8 Mar 02 date

Acknowledgments

I would like to express my sincere appreciation to my advisor and advisory committee chairman, Dr. Michael Shelley, for his guidance and support throughout the course of this thesis effort. Your patience, insight, and support were paramount to the success of this endeavor.

Additionally, I would like to thank my advisory committee members, Dr. Charles Bleckmann, Dr. Mark Goltz, and Dr. James Amon, for their expertise and support. Your contributions were greatly appreciated,

Finally, I would like to thank my wife for her unwavering love and support. I could not have done this without you and look forward to many, many happy years together. My thanks also go out to my family and friends whose support and encouragement are always greatly appreciated.

Jason S. Campbell

Table of Contents

Page

List of Figures

List of Tables

Abstract

The purpose of this study is to compare different approaches to modeling the reductive dechlorination of chlorinated ethenes in the anaerobic region of an upward flow constructed wetland by microbial consortia. A controlled simulation experiment that compares three different approaches to modeling the degradation of chlorinated ethenes in wetland environments is conducted and investigates how each of the modeling approaches affect simulation results.

Concepts like microbial growth in the form of a biofilm and spatially varying contaminant concentrations bring the validity of the CSTR assumption into question. These concepts are incorporated into the different modeling approaches to evaluate the CSTR assumption.

Model simulations show that spatially varying contaminant concentrations have a significant affect on contaminant effluent concentrations. Additionally, the significance of the incorporation of a biofilm concept depends on the time characteristics of both diffusive mass transport and reaction kinetics.

A COMPARISON OF MODELING APPROACHES IN SIMULATING CHLORINATED ETHENE REMOVAL IN A CONSTRUCTED WETLAND BY A MICROBIAL CONSORTIA

I. Introduction

Chlorinated ethenes and their natural transformation products represent the most prevalent organic groundwater contaminants in the country (McCarty, 1996). Only in the past 20-25 years has it been discovered that microbial activity in natural wetland environments can degrade these compounds to innocuous end products. This knowledge, coupled with new technologies in microbiology and the environmental sciences, has inspired researchers to investigate the microbial processes and interactions that lead to the bioremediation of chlorinated ethenes. One area of research focuses on using constructed wetland environments to remediate groundwater contaminated with chlorinated ethenes.

Background

Over the past three decades, the United States Air Force (USAF) and the Department of Defense (DoD) have identified thousands of sites containing groundwater contaminated with chlorinated ethenes such as Perchloroethene (PCE), Trichloroethene (TCE), isomers of Dichloroethene (DCE), and Vinyl Chloride (VC). Both PCE and TCE are widely used as industrial solvents to clean grease from metal parts, and are used in the production of various consumer products. Additionally, PCE is used in the dry-cleaning industry. Dichloroethene is also used as an industrial solvent and in the production of certain flexible plastics. Vinyl Chloride is primarily used in the production of polyvinyl chloride (PVC), a plastic used to make pipes, wire coatings, and packaging material.

There are several ways in which chlorinated ethenes like PCE, TCE, DCE, and VC can get into groundwater, such as careless use and disposal practices, leakage from underground storage tanks and landfills, and through the breakdown of other chlorinated ethenes. Due to their relatively low solubility in water and high densities, chlorinated ethenes tend to remain in a nonaqueous-phase liquid (NAPL) form that sinks to the bottom of an aquifer. However, a portion of the NAPL does solubilize and significant concentrations of chlorinated ethenes can be found in groundwater. Once solubilized, the contaminant moves through the aquifer with the groundwater, sorbing and desorbing to the soil, and creating a plume of contaminant with decreasing concentration as it flows further from the source of contamination.

Implications of human exposure to chlorinated ethenes vary from compound to compound. The International Agency for Research on Cancer (IARC) has determined that both PCE and TCE are probable human carcinogens and can cause damage to the liver and kidney at high dose levels (Agency, 2001). While DCE has not been deemed a probable human carcinogen due to a lack of significant evidence, it has been found to be associated with liver and kidney damage (Agency, 2001). On the other hand, VC is a known human carcinogen that causes a myriad of other problems (Agency, 2001). High levels of VC exposure can cause liver, kidney, heart, lung, and nerve damage as well as prevent blood clotting (Agency, 2001). These compounds have become such a problem in the environment that the Agency for Toxic Substances and Disease Registry (ATSDR) has listed VC and TCE as two of their Top 20 Hazardous Substances (Agency, 2001). It is apparent that high levels of exposure to any of these chemicals can be harmful, if not

fatal, to humans, and sites containing chlorinated ethenes must be remediated to safe levels.

The most popular form of chlorinated ethene remediation is the pump-and-treat method. In fact, approximately 89% of all groundwater-contaminated sites use this technology today (National Research Council, 1999). The pump-and-treat method utilizes several different on-site treatment technologies like air strippers and bioreactors to remove chlorinated ethenes from groundwater.

Air strippers remove chlorinated ethenes from groundwater by cascading the water over a series of baffles, thus increasing the surface area of water that is exposed to the air and volatilizing the contaminant. Now that the chlorinated ethene is in a gaseous form, Clean Air Act (CAA) regulations require that air expelled from air strippers be filtered using either a carbon filter or a biofilter (Sayles, 1993). The effluent from an air stripper is either returned to the aquifer or allowed to run off into a stream or lake.

A bioreactor is a vessel in which biological reactions are carried out by microorganisms or enzymes contained within the vessel (Armenante, 1993). Examples of the types of bioreactors in use today are the agitated, surface-aerated, rotating-disc, packed-bed, and fluidized-bed bioreactors.

Use of air strippers and bioreactors require large amounts of energy and maintenance to reduce contaminant levels to Environmental Protection Agency (EPA) standards. Additionally, extraction and treatment equipment are costly capital investments that require constant maintenance and repair.

As stated earlier, chlorinated ethenes are relatively insoluble in water; so, depending on the size and amount of contamination, remediation of groundwater

contaminated with chlorinated ethenes can last many years or even decades. Due to long remediation times and the current energy and equipment intensive remediation methods, the cost of remediating just one contaminated site can be in the tens of millions of dollars.

The USAF currently uses the pump-and-treat remediation method at the majority of its groundwater remediation sites. To date, the AF has spent hundreds of billions of dollars on treating sites contaminated with PCE and TCE. With many sites still on the clean-up list, the AF will spend billions more to treat these sites using current technology. In the quest for cheaper, more efficient, and effective methods of contaminant remediation, it has been discovered that natural wetland environments can completely degrade chlorinated ethenes to innocuous end products like carbon dioxide (CO_2) and water (Lorah and Olsen, 1999).

Wetland environments are complex ecosystems containing many microbial populations that assist and facilitate the degradation of contaminants. Regions within a wetland may be classified as either aerobic or anaerobic. The aerobic region is the top layer of the wetland containing plant roots that supply the region with oxygen. The anaerobic region is the bottom layer of the wetland and contains no oxygen. Each region hosts various populations of microorganisms that perform different metabolic processes that directly or indirectly degrade contaminants flowing through the wetland. The degradation pathway of PCE in a wetland environment is first to TCE, then to isomers of DCE, to VC, to ethene, and finally to CO_2 and water. Some microbial populations can degrade these chlorinated ethenes directly to CO_2 and water, skipping the subsequent compounds in the degradation pathway (Lee et al., 1998).

Four main degradation processes govern the degradation of chlorinated ethenes: energy-yielding oxidations, co-metabolic oxidations, energy-yielding reductions, and co-metabolic reductive dehalogenation (Lee et al., 1998). Energy-yielding oxidations occur in either the aerobic or anaerobic region when certain microbial populations use chlorinated ethenes as a primary energy source for cell growth and maintenance. Co-metabolic oxidations are another aerobic degradation process in which enzymes produced by microorganisms act on a primary substrate, such as methane, fortuitously degrade chlorinated ethenes (Lee et al., 1998). Energy-yielding reductions occur in the anaerobic region and are similar to the energy-yielding oxidation process except that the chlorinated contaminant is used as an electron acceptor instead of an electron donor. Co-metabolic reductive dehalogenation also occurs in the anaerobic region and appears to be a side-reaction carried out by many types of anaerobic microorganisms, including methanogens, sulfate-reducing bacteria (Bagley and Gossett, 1989), and novel bacteria types that do not fall into either category (Maymo-Gatell et al, 1995).

Of particular interest to this research effort are the reductive dehalogenation processes that occur in the anaerobic region of a wetland environment. Because groundwater and sediment microenvironments are frequently limited in oxygen (anaerobic), it is generally believed that reductive dehalogenation is a key initial biological step to achieve biodegradation of highly chlorinated compounds in these environments (Lee et al., 1998).

Previous research conducted by Captain Colby Hoefar (2000) developed a fundamental model of the degradation of chlorinated ethenes in a constructed wetland. His thesis, "Modeling Chlorinated Ethene Removal in Constructed Wetlands: A System

Dynamics Approach", took a macroscopic look at the degradation of chlorinated ethenes in constructed wetlands, but additional detail was needed in describing the microbial interactions and processes in the methanogenic, or anaerobic, region.

Captain Randy Roberts (2001) followed Hoefar's work with his thesis, "Modeling Chlorinated Ethene Removal in the Methanogenic Zone of Constructed Wetlands: A System Dynamics Approach". This model investigated the microbial interactions and competition in the anaerobic region, adding further detail to constructed wetland research and modeling efforts.

Both of these models conceptualized the different regions of the wetland as continuously stirred tank reactors (CSTR) as a modeling simplification. Intuitively, this assumption appears flawed because one can reason that microbial activity in one region of the wetland will decrease contaminant concentrations for subsequent regions. It is conceivable to consider that contaminant concentrations vary not only temporally, but spatially as well.

Additionally, the models developed by Hoefar and Roberts describe the microorganisms as being suspended in the aqueous phase. In flowing systems, there is a continuous input of nutrients that encourages rapid growth and reproduction of colonizing bacteria and the eventual buildup of biofilms (Marshall, 1997). Modeling bacteria as a biofilm has implications regarding the bioavailability of contaminants to microorganisms for degradation. Suspended microorganisms are modeled as having direct access to contaminants as they surround them in the aqueous phase. On the other hand, biofilms require that the contaminant be transported to the microorganisms through a mass transfer process that could limit the amount of degradation taking place. Thus,

contaminants are more bioavailable to microorganisms suspended in the aqueous phase as opposed to microorganisms contained within a biofilm.

The possibility of spatially varying contaminant concentrations and biofilm mass transfer limitations leads us to believe that the CSTR simplification may be flawed in the context of a constructed wetland. Perhaps a modeling approach that allows for spatially varying contaminant concentrations and mass transfer limitations may be more appropriate when modeling the degradation of chlorinated ethenes within a wetland environment.

Problem Statement

The purpose of this study is to compare different approaches to modeling the reductive dechlorination of chlorinated ethenes in the anaerobic region of an upward flow constructed wetland by microbial consortia. A controlled experiment that compares three different approaches to modeling the degradation of chlorinated ethenes in wetland environments will be conducted and will investigate how each of the modeling approaches affect simulation results. Model #1 will model degradation using the CSTR assumption and will be the baseline model for this study, Model #2 will use a tanks-in-series approach to simulate the spatial variation in contaminant concentrations, and Model #3 will incorporate a biofilm concept that will introduce a mass transfer process that can limit contaminant degradation processes.

Coupled with the research of Hoefar and Roberts, a comprehensive model predicting the degradation of chlorinated ethenes in a constructed wetland could be formulated and used to assist engineers in the design and construction of remediation wetlands.

Research Questions

1. What effect does a spatially varying contaminant concentration have on effluent concentrations?

2. What modeling approach best represents a biofilm concept as the degradation mechanism in a constructed wetland?

3. How do the biofilm models compare to the CSTR and Tanks-in-series models? Does the biofilm concept have any effect on effluent concentrations or can the CSTR simplifying assumption be tolerated in accurately studying the dynamics of the system?

4. What simplifying assumptions regarding biofilm contaminant transport and reaction kinetics can be tolerated in accurately studying the dynamics of the system?

Scope/Limitations

This study is limited to investigating the degradation of PCE, TCE, DCE, and VC in the anaerobic region of a constructed wetland. The effects of pH and temperature on microbial activity will not be addressed in this study. An additional assumption will be that the anaerobic region has been depleted of all other electron acceptors and methanogenic conditions exist. Further, this work will be based on one of the upward flow constructed wetland treatment cells at Wright-Patterson Air Force Base (AFB), OH. These wetland treatment cells were built by the USAF and are being used by the Air Force Institute of Technology (AFIT) in conjunction with Wright State University to explore the use of constructed wetlands as a remediation tool for groundwater contaminated with chlorinated ethenes.

II. Literature Review

Introduction

The pump-and-treat method of remediation utilizes two basic methods to remove chlorinated ethenes from groundwater. The first method uses physical processes to separate the contaminant from the groundwater. An example of a physical method would be using an air stripper to volatilize chlorinated ethenes from contaminated groundwater. The second method uses bioreactors that utilize biological processes to remove the contaminants. Biological processes in bioreactors are carried-out by various populations of microorganisms. There are many kinds of bioreactors, most incorporating some type of mechanical system like mixers or aerators to facilitate the degradation of contaminants. A constructed wetland is basically another form of a bioreactor except that it doesn't need mechanical systems to aid in the degradation of contaminants, like chlorinated ethenes, because wetland sediments naturally contain the nutrients needed for biodegradation processes. With its self-sustaining nature and limited use of mechanical components, a constructed wetland is an inexpensive, low maintenance alternative to other treatment methods currently in use.

Three main processes that govern the removal of contaminants from wetland environments are biological, chemical, and physical processes. Plants and microorganisms are the main contributors to biological processes in wetlands. Depending on the plant species and type of contaminant, plants can remove contaminants from wetland environments by either storing them in their tissues, biochemically transforming them, or transpiring them to the atmosphere (Jones et. al., 2000). Some microorganisms can either directly or indirectly facilitate the removal of chlorinated

ethenes from groundwater during metabolic processes. Chemical processes that contribute to the removal and reduction of contaminants from wetland environments include redox reactions, adsorption, precipitation, chelation, and photolysis (Jones et. al., 2000). Processes like dilution, volatilization, and deposition are all physical processes that aid in the removal of contaminants from wetland environments by either reducing concentrations below toxic levels, allowing biodegradation to occur, or by storing the contaminant in another phase that may or may not be more accessible to microorganisms. Biodegradation is a combination of microbial metabolic processes and redox reactions catalyzed by microbial activity.

Wetland environments provide excellent conditions for many different types of aerobic and anaerobic microbial populations to thrive. Each type of microorganism utilizes different substrates to gain energy for cell growth and maintenance. In most microenvironments, a consortium of microorganisms exist in a symbiotic relationship and supply one another with energy-yielding substrates. A biofilm forms when multiple layers of microorganisms embedded in a polymer matrix develop at a surface (Marshall, 1997). Biofilms play a central role in the degradation of organic substances in biotechnological processes as well as in natural ecosystems (Characklis, 1990). Much research has been done in microbiology on the interactions between microorganisms and how they grow to form biofilms in the environment. One way to conceptualize microbial growth in a wetland environment is to think of microorganisms forming biofilms on wetland soil particles. The degradation of contaminants in the water flowing through the wetland would then be a function of the contaminant diffusing into the biofilm and the various redox reactions catalyzed by the different populations of microorganisms

contained within the biofilm. It has been estimated that approximately 80 to 90% of the cells in a porous medium are sorbed to solid surfaces and the remainder are free-living (Maier et. al., 2000). Consequently, microorganisms attached to soil particles in the form of biofilms will carry out the majority of biodegradation.

Constructed Wetland Environments

Wetland environments exist in a wide range of types, sizes, and geographic locations but it is the co-occurance of three common characteristics that distinguish wetland environments from other types of ecosystems:

1) Standing water (inundation) or high water table (saturation) for some period of the biological growing season

2) Hydric soils that provide a predominantly anaerobic environment for chemical and biological processes

3) Specialized plants (hydrophytes) adapted to periodic or permanent inundation or saturation (Jones et. al., 2000).

The two basic types of wetland systems are free water surface (FWS) systems and subsurface flow (SF) systems (Maier et. al., 2000). Like the name implies, FWS systems have a water surface that is exposed to the atmosphere and tend to be fed from surface water sources like storm water run-off, streams, and precipitation. On the other hand, SF systems contain a water surface that is below the ground surface and tend to be groundwater fed. The type and extent of biological, chemical, and physical processes, as well as the type and number of plant species, occurring in a particular wetland, are highly dependent on the hydrology of the wetland (Jones et. al., 2000).

The wetland test cells that have been constructed at Wright-Patterson AFB in Dayton, Ohio are hybrids of both the FWS and SF systems. The test cells have the FWS

system characteristic of water surfaces that are exposed to the atmosphere while also having the SF system characteristic of being primarily fed from an underground source. However, unlike typical SF systems that are fed from horizontal groundwater flow, the test cells experience an upward groundwater flow as the water is pumped into the bottom of the test cell. Figure 2.1 is a cross-sectional view of the Wright-Patterson constructed wetland test cell #1:

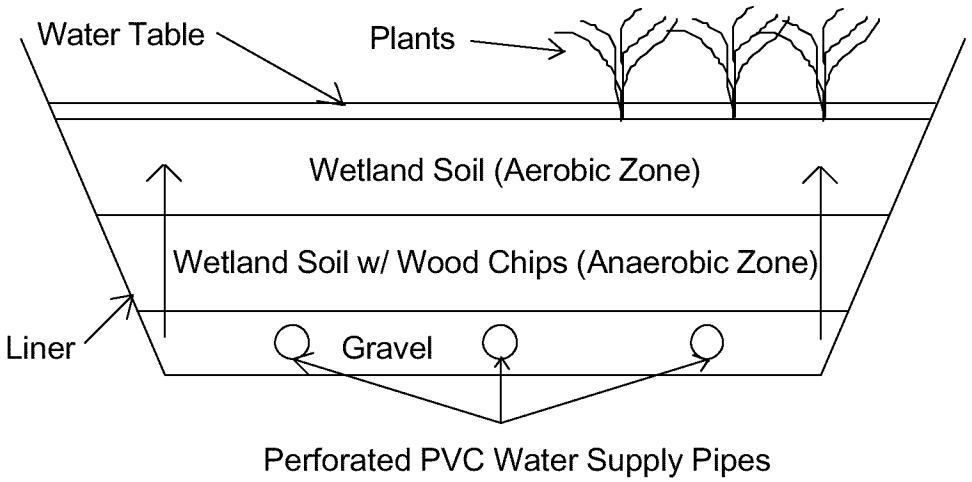


Figure 2.1. Constructed wetland test cell #1 cross-section, Wright-Patterson AFB, OH (not to scale).

Water is pumped from a contaminated groundwater source nearby into the bottom of the wetland test cell through perforated PVC pipes embedded in an 18-inch layer of gravel. The purpose of the gravel layer is to distribute the water evenly in an effort to create a constant, steady flow through the whole cross-section of the wetland test cell. After flowing through the gravel layer, the water flows upward through an 18-inch layer of typical wetland soil that has been augmented with wood chips. This layer is referred

to as the anaerobic region due to the lack of sufficient levels of oxygen available for aerobic microbial processes. The wood chips provide the organic material necessary to start and sustain anaerobic microbial processes. Next, the water flows through a 36-inch layer of typical wetland soil without wood chip augmentation. Planted in this layer are various species of wetland, or hydrophytic, vegetation that supply oxygen deep into the layer through their roots. Because most of this top layer is supplied with oxygen, it is referred to as the aerobic region, though some areas may not be supplied with oxygen. A geomembrane liner has been installed to contain the test cell material and prevent contaminated groundwater from reentering the natural environment. Test cell #2 is comprised of three layers of soil; an 18-inch layer of typical wetland soil on the bottom, an 18-inch layer of iron-rich soil in the middle, and an 18-inch layer of typical wetland soil on the top. None of the layers of soil in test cell #2 have been augmented with wood chips.

Microbial Processes

The process thought to dominate the degradation of chlorinated ethenes in the anaerobic region of wetland environments is reductive dechlorination (Lee et al., 1998). Halogenated compounds, like chlorinated ethenes, are undoubtedly removed by natural remediation processes, either through halorespiration or co-metabolism (Bleckmann et. al., 2000). The type of reductive dechlorination that occurs is dependent upon the types of microorganisms living in the soil and the compounds or nutrients available to those microorganisms. Research has shown that highly chlorinated contaminants such as PCE and TCE will be more rapidly degraded anaerobically; whereas, less chlorinated species,

such as DCE and VC, may be longer lived in anaerobic environments and more readily degraded by aerobic processes (Lee et al., 1998; Vogel et al., 1987).

Anaerobic Energy-Yielding Reductive Processes

Energy-yielding reductive degradation processes, often referred to as dehalorespiration or halorespiration, result when microorganisms use a halogenated contaminant as an electron acceptor in oxygen limited environments to gain energy for cell synthesis and maintenance during metabolic processes (Lee et al., 1998; McCarty, 1997). Depending on the species, these microorganisms may produce cis-DCE as a final end product or may carry out complete dechlorination to ethene (Lee et al., 1998). In order for halorespirators to thrive, certain environmental conditions must exist and certain electron donors must be present. Figure 2.2 depicts the processes that must occur to create the proper conditions for halorespiration.

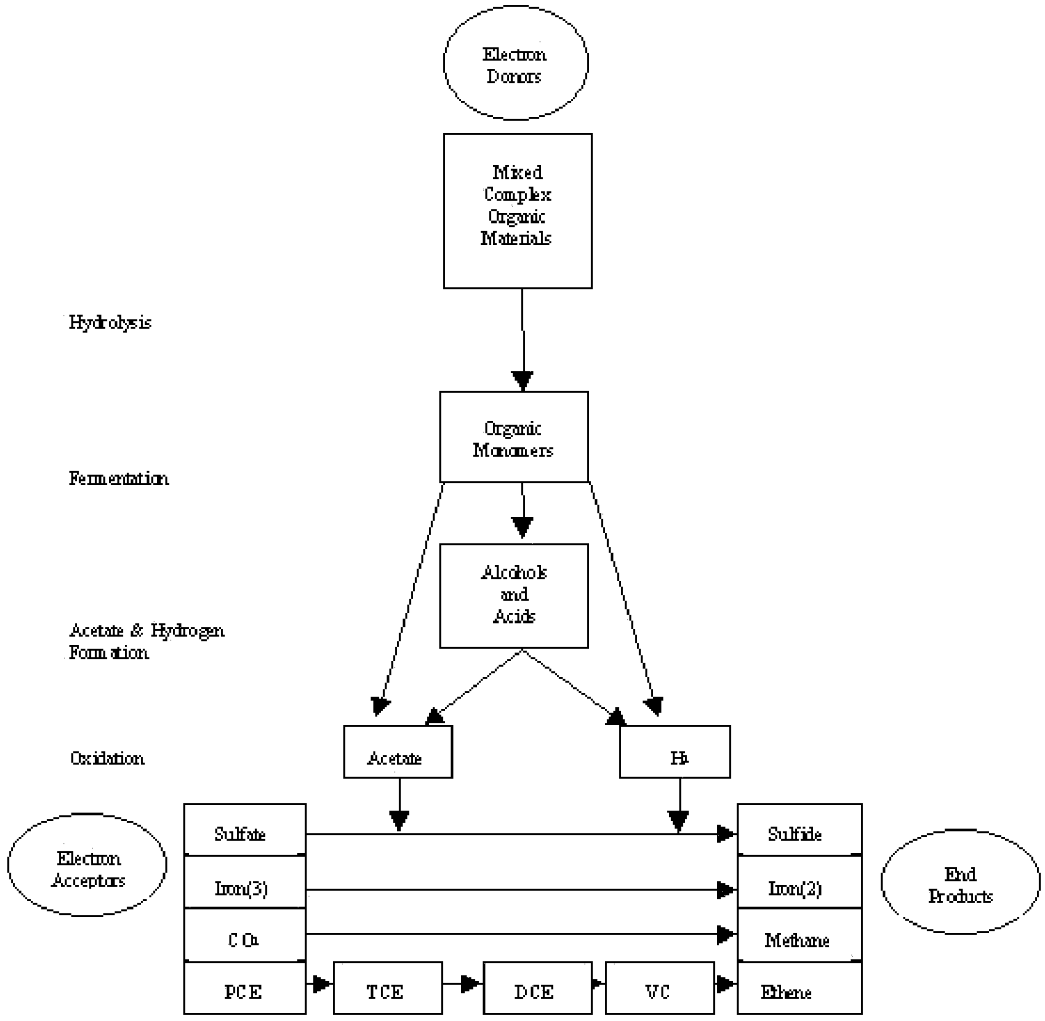


Figure 2.2. Electron flow from electron donors to electron acceptors in the anaerobic oxidation of mixed complex organic materials. Microorganisms that can use chlorinated compounds (PCE, TCE, cis-DCE, and VC) as electron acceptors in halorespiration compete for the electrons in the acetate and hydrogen intermediates with microorganisms that can use sulfate, iron (III), and CO_2 as electron acceptors (McCarty, 1997).

The chain of processes starts out with a population of microorganisms that can hydrolyze organic material found in the soil, producing organic sugars. Another microbial population then ferments the organic sugars to produce alcohols and organic acids. The alcohols and organic acids are then used by another microbial population as electron donors in their metabolic processes and produce acetate and hydrogen. Next,

sulfate-reducing microorganisms use the acetate and hydrogen as electron donors for their metabolic processes. When sulfate concentrations are reduced low enough, iron-reducing microorganisms compete with the sulfate-reducers for acetate and hydrogen electrons. Similarly, when iron concentrations are reduced to a certain level, methanogens compete with the sulfate- and iron-reducers for acetate and hydrogen electrons. Finally, when sulfate, iron, and carbon dioxide are either non-existent or remain only in very low concentrations, halorespirators successfully compete for acetate and hydrogen electrons to be used in metabolic processes. Conditions are now optimal for the degradation of chlorinated ethenes.

Anaerobic Co-Metabolic Reductive Processes

Co-metabolic reductive degradation processes result when a contaminant is fortuitously transformed by enzymes which microorganisms are using for other purposes (McCarty, 1996). Certain species of methanogens, sulfate-reducing bacteria, and novel microbial types that do not fall into either category are thought to carry out reactions that are not energy-yielding but rather co-metabolic because only a small fraction of the total reducing equivalents derived from the oxidation of electron donors is used to reduce the contaminant (Lee et. al., 1998). Again, appropriate environmental conditions must exist to allow the chain of processes explained and depicted above in Fig. 2.2 to be carried out so that sufficient amounts of acetate and hydrogen can be produced to support these co-metabolic methanogens, sulfate-reducing, and novel types of microbial populations.

Biofilm Modeling

Conceptually, substrate removal from an aqueous phase requires diffusion of all metabolic reactants into the biofilm, metabolism by the organisms, and diffusion of the

metabolic products back through the biofilm and into the aqueous phase (Williamson and McCarty, 1976). This basic rationale has been used extensively over the past 25 years in research involving the removal of aqueous phase substrates by biofilms (Rittmann and McCarty, 1978, 1980, 1981; Suidan and Wang, 1985; Wang, Suidan, and Rittmann, 1986; Saez and Rittmann, 1987; Dykaar and Kitanidis, 1996; Polprasert, Khatiwada, and Bhurtel, 1998; MacDonald et. al., 1999). Figure 2.3 is the conceptual biofilm model that will be used in this research.

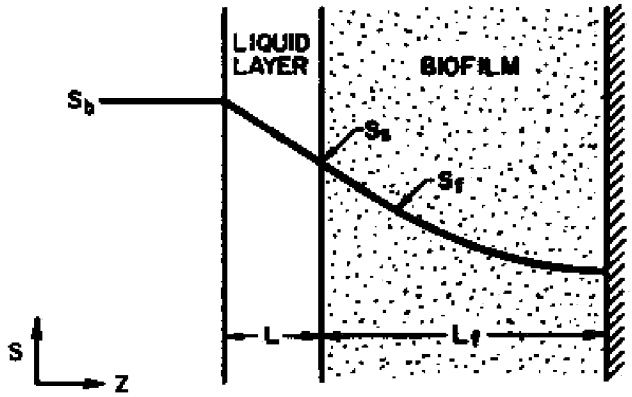


Figure 2.3. Schematic of Substrate Distribution in a Planar Biofilm (Suidan and Wang, 1985).

The steady state substrate flux though the stagnant liquid layer, L (L), is determined by multiplying the substrate concentration gradient between the bulk liquid phase, S_b (M/L^3), and the biofilm surface, S_s (M/L^3), by the substrate mass-transfer coefficient, k_c (L/T)

$$J_s = k_c(S_b - S_s) \quad \textbf{(2.1)}$$

where J_s is the substrate flux per unit area of biofilm through the stagnant liquid layer (M_S/L^2-T). An important part of the biofilm model is the explicit incorporation of mass-

transport resistance from the bulk liquid, through the stagnant liquid layer, and to the biofilm surface (Rittmann and McCarty, 1981). Mass-transport resistance is expressed here by using a mass-transfer coefficient which can be calculated by dividing the molecular diffusion coefficient of the substrate through water by the stagnant liquid layer thickness, L (Rittmann and McCarty, 1978, 1980, 1981; Suidan and Wang, 1985; Wang et. al., 1986; Saez and Rittmann, 1987; MacDonald et. al., 1999); L is defined as the equivalent depth of liquid through which the actual mass transport can be described by molecular diffusion alone (Rittmann and McCarty, 1981).

$$k_c = \frac{D}{L} \qquad \textbf{(2.2)}$$

The following equation is used to estimate the thickness of the stagnant liquid layer for each substrate:

$$L = \frac{D(\mathrm{Re}_m)^{3/4}(Sc)^{2/3}}{5.7v} \qquad \textbf{(2.3)}$$

where D is the molecular diffusion coefficient of the substrate through water (L^2/T); Re is the Reynolds number as defined by Equation 2.4 (unitless); Sc is the Schmidt number as defined by Equation 2.5 (unitless); and v is the average bulk water velocity (L/T) (MacDonald et. al., 1999). The Reynolds number and Schmidt number are defines as follows:

$$\mathrm{Re}_m = \frac{2\rho_w d_p v}{(1-n)\mu} \qquad \textbf{(2.4)}$$

$$Sc = \frac{\mu}{D\rho_w} \qquad \textbf{(2.5)}$$

where ρ_w is the density of water (M/L^3); d_p is the diameter of the soil particles (L); n is the porosity of the soil (unitless); and μ is the dynamic viscosity of water (M/L-T).

Substrate utilization at any point in the biofilm is assumed to follow a Monod relation (Williamson and McCarty, 1976; Rittmann and McCarty, 1978, 1980, 1981; Suidan and Wang, 1985).

$$\frac{dS_f}{dt} = -\frac{kX_f S_f}{K_s + S_f} \quad \text{.....(2.6)}$$

Here, S_f is the substrate concentration (M/L^3) at any depth Z in the biofilm; k is the maximum substrate utilization rate (T^{-1}); X_f is the uniform microbial concentration in the biofilm (M/L^3); and K_s is the Monod half-velocity coefficient for the substrate (M/L^3).

The decreasing substrate concentration at the biofilm surface, due to substrate utilization, is the driving force behind mass transfer in the biofilm model. As the substrate concentration in the biofilm decreases, the concentration gradient between the bulk liquid and the biofilm increases, thus creating a condition where more substrate will be transported into the biofilm through the molecular diffusion process described in Equation 2.1. Additionally, daughter product production (TCE, DCE, VC, and Ethene) is also determined with the Monod relationship using a mass conversion factor, f (unitless), that converts moles of parent compound degraded to moles of daughter product produced.

In their 1978 article entitled "Variable-Order Model of Bacterial-Film Kinetics", Rittmann and McCarty use the same conceptual model used for Model #3 but take their analysis one step further and derive an analytical solution that solves for the flux of substrate into a biofilm where it is then degraded via a Monod relationship. Some

assumptions that they make for this model is that the biofilm is "deep", meaning that the concentration within the biofilm goes to zero before it reaches the particle surface on which the biofilm is attached. Additionally, they define several dimensionless variables in an effort to reduce the number of independent variables involved in the solution. Equations 2.7 thru 2.9 are three of the dimensionless variables used in the final solution

$$S^* = \frac{S}{K_s} \quad \textbf{(2.7)}$$

$$D_f{}^* = \frac{D_f}{D} \quad \textbf{(2.8)}$$

$$L^* = \frac{L}{\tau} \quad \textbf{(2.9)}$$

where S^* is the dimensionless substrate concentration; S is the substrate concentration in the bulk liquid phase (M/L^3); D_f^* is the dimensionless biofilm diffusivity; D_f is the biofilm diffusivity (L^2/T); L^* is the dimensionless diffusion-layer depth; and τ is the standard depth dimension (L) as defined by Equation 2.10 (Rittmann and McCarty, 1978).

$$\tau = \sqrt{\frac{2K_s D_f}{kX_f}} \quad \textbf{(2.10)}$$

Before the mass flux can be calculated, the following parameters need to be defined:

$$\Lambda = \ln(S^*) - \ln\left(2 + \frac{\ln\left(D_f{}^*\right)}{2.303}\right) - 1.8\ln\left(1 + 2L^* D_f{}^*\right) + 3.53 \quad \textbf{(2.11)}$$

$$q = 0.75 - 0.25\tanh\left(0.477\Lambda\right) \quad \textbf{(2.12)}$$

$$C^* = \frac{2D_f^*\left(\sqrt{2}+2L^*D_f^*\right)^{(1-q)}}{1.0+0.54\left(1+0.0121\ln\left(1+2L^*\right)\right)\left(1-8.325\left(\ln\frac{q}{0.707}\right)^2\right)} \quad \textbf{(2.13)}$$

$$\left(\frac{J}{A}\right)^* = C^*(S^*)^q \quad \textbf{(2.14)}$$

Equations 2.11 thru 2.14 comprise the variable order model solution in which q is the reaction order (unitless) and C* is the dimensionless reaction coefficient (Rittmann and McCarty, 1978). The actual flux per unit surface area, (J/A) (M/L^2-T), is related to the dimensionless flux per unit surface area, $(J/A)^*$, according to Equation 2.15 (Rittmann and McCarty, 1978).

$$\left(\frac{J}{A}\right) = \left(\frac{J}{A}\right)^*\left(\frac{DK_s}{\tau}\right) \quad \textbf{(2.15)}$$

With this model, the steady-state contaminant mass-flux into the biofilm can be found for any given contaminant concentration. Additionally, Rittmann and McCarty went on to solve the steady-state contaminant concentration equations for both the complete-mix (CSTR) and the plug-flow reactors. Equations 2.16 and 2.17 are the steady-state equations for the complete-mix reactor and Equation 2.18 solves for the reaction coefficient

$$S = S_o - \left(\frac{a}{Q}\right)CS^q \text{; when q < 1} \quad \textbf{(2.16)}$$

$$S = \frac{S_o}{1+\frac{a}{Q}C} \text{; when q = 1} \quad \textbf{(2.17)}$$

$$C = \frac{C^*DK_s^{(1-q)}}{\tau} \quad \textbf{(2.18)}$$

where S_o is the influent concentration (M/L^3); C is the variable-order reaction coefficient for the qth-order reaction; *a* is the specific surface area (biofilm surface area per unit reactor volume) (L^{-1}); and Q is the hydraulic loading rate (flow rate per unit reactor volume) (T^{-1}) (Rittmann and McCarty, 1978).

Equations 2.19 and 2.20 solve for the steady-state contaminant concentration in a plug-flow reactor using the specific surface area, *a* (L^{-1}), and the surface loading rate (flow rate per unit cross-sectional area), *v* (L/T),

$$S = S_o e^{\left(\frac{-Cax}{v}\right)} \quad \textbf{(2.19)}$$

$$S = \left[\left(S_o\right)^{(1-q)} - \frac{Cax(1-q)}{v} \right]^{1/1-q} \quad \textbf{(2.20)}$$

where S>0 and x is the distance along the reactor (L).

III. Methodology

Introduction

One way to model the complex processes in a wetland system is to envision the system mechanistically. That is, the complete wetland system must be segregated into the components that most influence the system behavior of interest. Having identified the most important components, the processes that occur within and between components must be defined. The sum of process interactions will ultimately determine the system behavior.

System dynamists study and model the behavior of complex systems using a mechanistic approach and have defined four phases of the modeling process. These phases are conceptualization, formulation, testing, and implementation. The structure of the methodology of this research will utilize the four system dynamics modeling process phases.

Conceptualization

Previous wetland models developed by Hoefar and Roberts used a simplifying assumption that treated each region of the wetland as a CSTR containing suspended microorganisms that degrade soluablized contaminants. This assumption postulates that all microorganisms in a particular region of the wetland, the anaerobic region for example, are exposed to the same contaminant concentration. Since the amount of degradation that takes place at any point in the wetland is dependent upon the contaminant concentration, the accuracy of the value of the contaminant concentration at any point in the wetland is very important.

Visualizing an upward flow wetland, like the one shown in Figure 2.1, it is conceivable that the contaminant concentration at the bottom of the anaerobic region is greater than the contaminant concentration at the top of the anaerobic region. The spatial variability of the contaminant concentration is due to microbial activity that reduces the contaminant concentration as the bulk water flows upward through the anaerobic region. Additionally, there is evidence that suggests that the majority of microorganisms in wetland environments are not suspended but are attached to soil particles in the form of a biofilm. The concept of wetland microbial growth in the form of a biofilm, that incorporates a diffusional element not considered in suspended microbial growth, coupled with a spatially and temporally varying contaminant concentration, brings the validity and accuracy of the CSTR assumption into question.

One way to assess the CSTR assumption is to compare mechanistic models of a constructed wetland that incorporate spatially varying contaminant concentrations and biofilm mass-transfer processes to a mechanistic CSTR model. However, before any models can be developed, a reference mode that represents the behavior of the system must be realized. Previous research by Capt. Hoefar and Roberts indicates that contaminant levels in a constructed wetland reach a steady-state condition after some period of time. The steady-state condition is rather intuitive.

Envision the wetland volume as a tank full of clean water that has an inlet and an outlet. Now consider that a certain contaminant concentration is pumped into the inlet of the tank and water is allowed to flow out of the outlet. Neglecting any degradation of the contaminant in the tank, one can envision the contaminant concentration increasing from its initial value of zero to a steady-state value equal to the inlet concentration. Now if

degradation of the contaminant in the tank is included, the contaminant concentration in the tank will still reach a steady-state value; however, because the contaminant is being degraded, the steady-state concentration will be less than the inlet concentration. It is conceivable that wetland systems will behave in much the same manner. As such, an approach to steady-state conditions will be used as the reference mode for this study. Figure 3.1 graphically depicts the classic approach to steady-state reference mode.

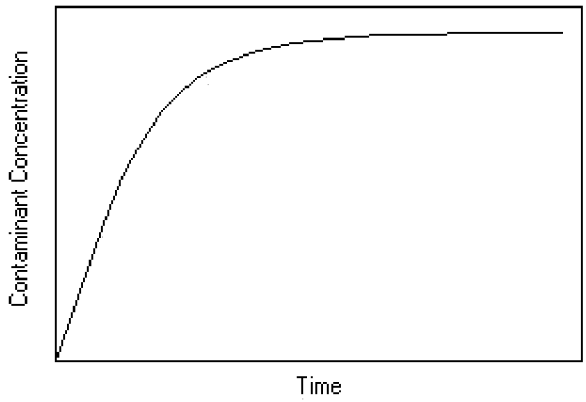


Figure 3.1. Reference Mode. Approach to Steady-State.

Formulation

The software used to develop the models for this research is STELLA 6.0.1 Research, developed by High Performance Systems. Using this software, one can mechanistically model complex systems using a series of stocks, flows, and parameters that provide conversion and definition. A stock is simply an accumulation of something in the system. In these models, the stock of interest is the mass of contaminant that is in the anaerobic region of the wetland. Flows move the contaminant in and out of the stocks as time passes. An example of a flow would be the amount of contaminated

groundwater that is coming into the anaerobic region per unit time. Finally, parameters are used to define flows. An example of a parameter would be the initial contaminant concentration of the influent.

Some general parameter values that are synonymous for all of the models being developed for this research are listed in Tables 3.1 and 3.2. Parameter values specific to a particular model will be listed in the section describing that model.

Table 3.1. Wetland Parameter Values Synonymous to all Models.

Parameter	**Value**	**Ref.**
Wetland Length	36.6 meters (120 feet)	1
Wetland Width	16.8 meters (55 feet)	1
Wetland Depth	.4572 meters (1.5 feet)	1
Soil Porosity	0.5	2
Soil Particle Diameter	1 mm	2
Wetland Flow	6.31×10^{-1} L/sec (10 gal/min)	1
Total Biomass, PCE	25,000 mg	3
Total Biomass, TCE	25,000 mg	3
Total Biomass, DCE	25,000 mg	3
Total Biomass, VC	25,000 mg	3
Initial PCE Concentration	5×10^{-4} mg/L	4
1. Value from Test Cell #1 at Wright-Patterson AFB, OH.		
2. Charbeneau, 2000		
3. Assumption based on Roberts, 2001		
4. Assumption based on Test Cell #1 at Wright-Patterson AFB, OH		

Table 3.2. Monod Kinetic Parameters for Biodegradation and Bioproduction

Parameter	Value	Ref.
k_{PCE}	8.292 x 10^{-5} mg PCE/mg Biomass-sec	1
k_{TCE}	1.095 x 10^{-4} mg TCE/ mg Biomass-sec	1
k_{DCE}	8.075 x 10^{-5} mg DCE/mg Biomass-sec	1
k_{VC}	5.21 x 10^{-5} mg/VC/mg Biomass-sec	1
$K_{s, PCE}$	.0896 mg PCE/L	1
$K_{s, TCE}$	.07096 mg TCE/L	1
$K_{s, DCE}$	.05233 mg DCE/L	1
$K_{s, VC}$	18.125 mg VC/L	1
f_{PCE}	.79222 mg TCE/mg PCE	2
f_{TCE}	.73772 mg DCE/ mg TCE	2
f_{DCE}	.64448 mg VC/mg DCE	2
f_{VC}	.44836 mg Ethene/mg VC	2
1. Fennel and Gossett, 1998		
2. Calculated using Periodic Table		

In addition to parameter values that hold true for all models developed in this research, there are some general assumptions that apply to all models that need to be stated. These assumptions are used to simplify the problem and focus on the objectives of the research. Since the validation, or invalidation, of the CSTR simplifying assumption is the main objective of this research, only the processes that set the CSTR model apart from the other models will be taken into consideration. Assumptions about all other processes occurring in a constructed wetland are listed below. Listed are general assumptions that hold true for all models developed in this research. Each model will have additional model-specific assumptions, which will be listed in the section describing that model.

1) Biomass growth will not be modeled and the amount of biomass available to degrade contaminants will be held at the same value (biomass growth equals biomass death).

2) The biomass is composed of four distinct populations of microorganisms, each capable of degrading only one of the contaminants (PCE, TCE, DCE, and VC).

3) Competition for electron donors will not be modeled, as there is an abundant supply to support degradation processes.

4) Sulfate, iron (III), and CO_2 have been reduced to low levels and methanogenic conditions exist, allowing biodegradation of chlorinated ethenes to occur.

Model #1 Concept and Formulation

Model #1 will be the baseline for this research. Previous efforts by Hoefar and Roberts modeled the entire anaerobic region, a layer of the wetland that is eighteen inches thick, as a CSTR. By doing this, they have assumed that the contaminant concentrations at the bottom of the anaerobic region are the same as the contaminant concentrations at the top of the anaerobic region. This assumption may over-simplify the system because, intuitively, contaminant concentrations in the bulk aqueous phase will decrease as the water flows upward through the wetland. Figure 3.2 illustrates the basic structure of the CSTR system.

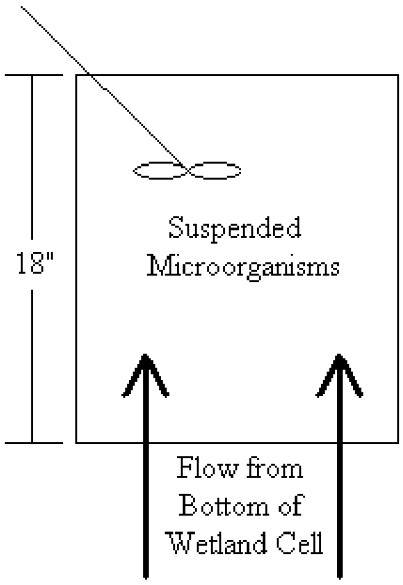


Figure 3.2. Basic schematic of Model #1. Contaminants flow in through the bottom of the layer and microorganisms suspended in the bulk aqueous phase degrade the contaminant. Contaminant that does not degrade flows out the top of the layer with convective flow. (not to scale)

Assumptions

In addition to the general assumptions stated above, a few assumptions specific to Model #1 are listed below.

1) The entire eighteen-inch depth of the wetland is modeled as a CSTR; so all concentrations are spatially constant.

2) Microorganisms are suspended in the aqueous phase and are evenly distributed throughout the wetland resulting in a uniform biomass concentration.

Parameters

Since Model #1 is the baseline model for this study, no additional parameters need to be defined at this point. The parameters listed in Tables 3.1 and 3.2 will be the only parameters used in this model.

Modeling Equations

Constructing Model #1, or the CSTR model, in STELLA is a simple exercise of employing the following mass balance equation

$$\frac{dM}{dt} = QS_o - QS - \frac{kX_{bio}S}{K_s + S} \quad \text{.....(3.1)}$$

where M is the bulk liquid contaminant mass (M); S_o is the influent contaminant concentration (M/L); Q is the wetland flow (L^3/T); S is the bulk liquid contaminant concentration (M/L^3); k is the maximum specific substrate utilization rate ($M_{substrate}/M_{biomass}$-T); X_{bio} is the uniform microbial mass in the bulk liquid (M); and K_s is the Monod half-velocity coefficient for the substrate (M/L^3).

The first and second terms to the right of the equal sign in Equation 3.1 are the contaminant mass-fluxes into and out of the anaerobic region due to convection, respectively. The third term in Equation 3.1 is the mass-flux of contaminant out of the anaerobic region due to degradation, which follows a Monod relationship.

In addition to modeling the degradation of contaminants, the model will also model the production of daughter products. The production of daughter products follows the same Monod relationship as did the contaminant degradation but a conversion factor is employed to convert moles of parent product degraded to moles of daughter product produced. This conversion factor is simply the ratio of the molecular weight of the daughter product to the molecular weight of the parent compound in the case of simple dehalogenation. Equation 3.2 defines daughter product production according to Monod kinetics

$$\frac{dM_{daughter}}{dt} = f\frac{k_{parent}X_{bio}S_{parent}}{K_{s,parent}+S_{parent}} \quad \text{.....(3.2)}$$

where f is the daughter product conversion factor (unitless).

Model Structure

Figure 3.3 shows the STELLA structure of Model #1.

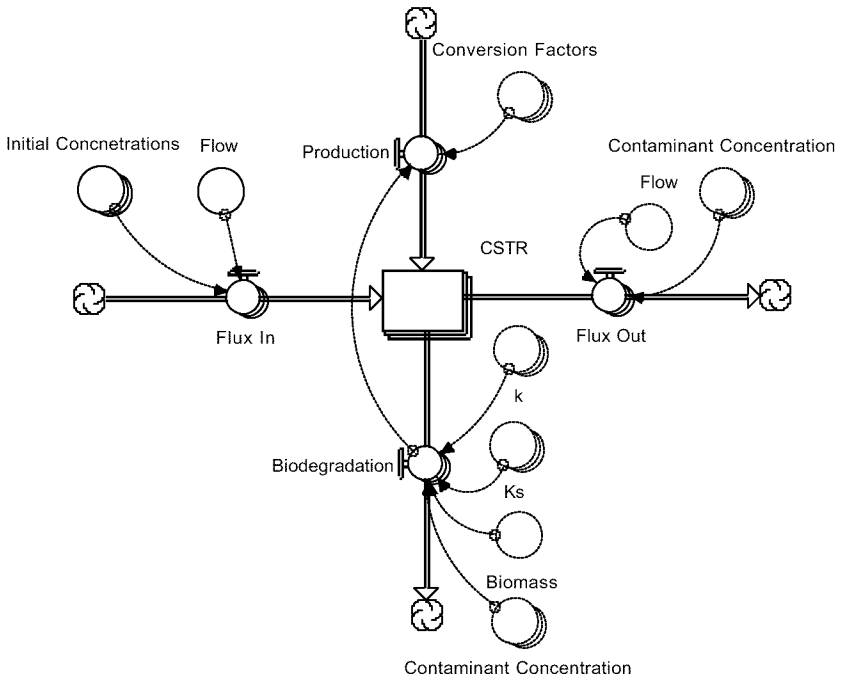


Figure 3.3. STELLA structure of Model #1.

The rectangle, referred to as a stock, in Figure 3.3 represents the entire anaerobic region that is being considered a CSTR in this model. The arrows going in and out of the stock represent the mass-flux of contaminants into and out of the system due to convective flow, biodegradation, or daughter product production. The circles in Figure 3.3 are the parameters that define the fluxes in the system.

Notice that the "biodegradation" mass-flux defines the "production" mass-flux. This mechanism is simulating the situation where daughter products are produced from

parent products. For example, the mass-flux of TCE being produced is equal to the mass-flux of PCE being degraded times the conversion factor, which converts moles of PCE into moles of TCE.

Model #2 Concept and Formulation

To model the spatial variation in contaminant concentration as it flows through the anaerobic region of the wetland, the region had to be discretized into many smaller sub-layers. Each of these sub-layers is assumed to be a CSTR. As designed, the model takes the form of a tanks-in-series system. Figure 3.4 depicts the basic structure of the tanks-in-series system.

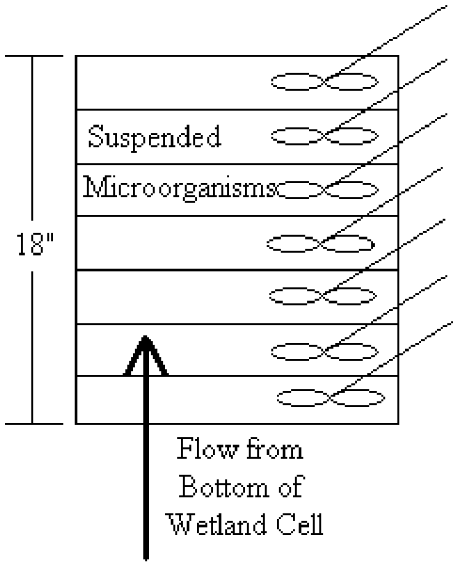


Figure 3.4. Basic schematic of Model #2. Contaminants flow in through the bottom of layer and microorganisms suspended in the bulk aqueous phase degrade the contaminant. Contaminant that does not degrade in the first layer flows out the top of the layer with convective flow into the next layer. As the bulk water flows from layer to layer, the contaminant concentration is decreased. (not to scale)

Assumptions

In addition to the general assumptions stated above, a few assumptions specific to Model #2 are listed below.

1) Each sub-layer, or tank, is modeled as a CSTR.

2) Microorganisms are suspended in the aqueous phase and are evenly distributed throughout each sub-layer resulting in a uniform biomass concentration throughout the entire wetland.

Parameters

In addition to the general parameters stated previously, Model #2 incorporates the parameters listed in Table 3.3.

Table 3.3. Additional Parameter Values for Model #2.

Parameter	Value	Ref.
Number of Sub-layers	18 layers	1
1. Value established by researcher		

Since this model is being discretized into many sub-layers, the total biomass for each sub-layer is equal to the total biomass for the wetland (100,000 mg) divided by the number of layers (18). Since there are four different microbial populations, the value for the total biomass in each sub-layer would be divided by four to determine the biomass of each microbial population in each sub-layer. This will ensure that Model #2 does not have more biomass than Model #1. Intuitively, if one model had more biomass then the other, biodegradation rate would be higher in one model as opposed to the other and the models could no longer be compared to one another.

Modeling Equations

The modeling equations used for Model #2 are the same as the equations used for Model #1. However, the equations will be applied to each individual sub-layer and will describe the mass-flux of contaminant from one sub-layer to the next. As a result, the mass-flux out of one sub-layer is the mass-flux into the next sub-layer and so on.

Model Structure

Figure 3.5 shows the STELLA structure of Model #2.

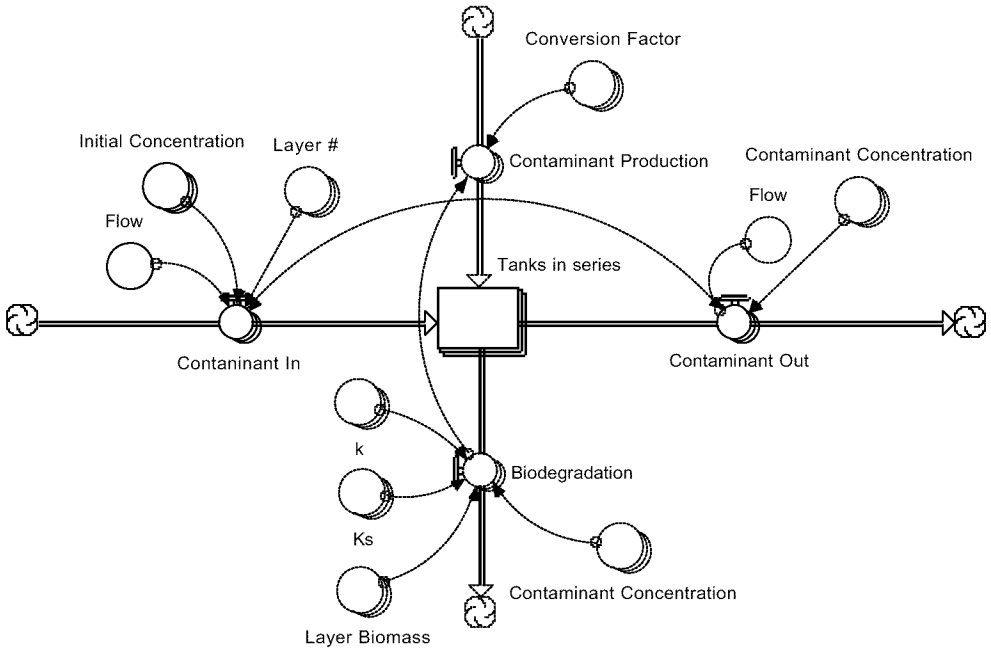


Figure 3.5. STELLA structure of Model #2.

Notice that the structure of this model is similar to that of Model #1. This is because it functions in much the same way but incorporates many sub-layers instead of just one large layer like Model #1. The one difference between this model and the model pictured in Figure 3.3 is that the "contaminant out" mass-flux defines the "contaminant

in" mass-flux. This is done to simulate the contaminant flowing from one sub-layer to the next.

Model #3 Concept and Formulation

Model #3 retains the discretization of Model #2 but will incorporate a biofilm phase into which the contaminants must diffuse before they can be degraded. The expectation is that the diffusion process will limit the amount of degradation that can occur, ultimately leading to simulation results that differ from those of Models #1 and #2. As presented in Chapter 2, the biofilm model will follow the concept shown in Figure 2.3 except that microbial and contaminant concentrations in the biofilm will be considered constant as stated in the assumptions below. Figure 3.6 is a macroscale schematic of the biofilm model.

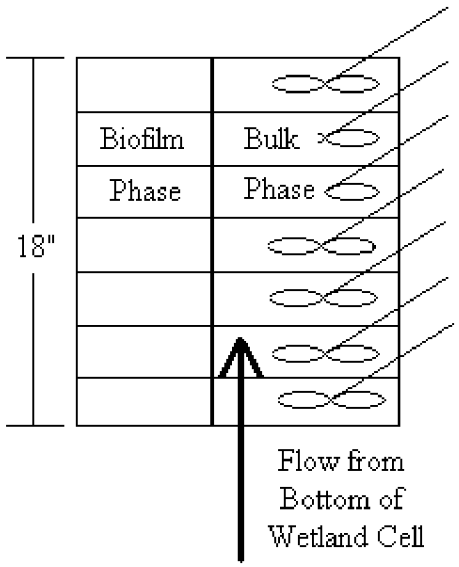


Figure 3.6. Schematic of Model #3. (not to scale)

Notice that the convective flow (represented by the arrow in Figure 3.6) is modeled only in the bulk aqueous phase in accordance with assumption #4 stated below. Also, both the bulk and biofilm phases are modeled as CSTRs.

Assumptions

Similar to the two previous models, Model #3 will also use the general assumptions stated earlier, but will need to incorporate some additional assumptions. Listed below are the modeling assumptions specific to Model #3.

1) The depth of the biofilm is considered constant since this research is not considering biomass growth. Additionally, a thin biofilm (approximately 1 micron) is assumed to simplify calculations.

2) Since the biofilm is thin, it is modeled as a CSTR. Thus the concentrations of substrates, contaminants, and biomass are uniform throughout the biofilm.

3) Biodegradation is defined by a Monod relationship and the kinetic parameters are constant throughout the biofilm resulting in a constant reaction rate.

4) Effects of longitudinal dispersion, diffusion, and convection within the biofilm are not accounted for in this model.

Parameters

In addition to the general parameters listed in Tables 3.1 and 3.2, Model #3 will also incorporate the additional parameters listed in Table 3.4.

Table 3.4. Additional Parameters for Model #3.

Parameter	Value	Ref.
$D_{w, PCE}$	8.2×10^{-10} m^2/sec	1
$D_{w, TCE}$	9.2×10^{-10} m^2/sec	2
$D_{w, DCE}$	1.12×10^{-9} m^2/sec	1
$D_{w, VC}$	1.23×10^{-9} m^2/sec	1
$D_{w, Ethene}$	2.0×10^{-9} m^2/sec	2
$k_{c, PCE}$	3.154×10^{-6} m/sec	3
$k_{c, TCE}$	3.407×10^{-6} m/sec	3
$k_{c, DCE}$	3.9×10^{-6} m/sec	3
$k_{c, VC}$	4.1×10^{-6} m/sec	3
$k_{c, Ethene}$	5.71×10^{-6} m/sec	3
Number of Sub-layers	18 layers	4
Biofilm Depth	1×10^{-6} m	5
Biofilm Coverage	50%	6
Biofilm Water Content	90%	7
1. Weidemeir, 1999		
2. Estimated using method from Schwarzenbach, 1993		
3. Calculated using method from MacDonald et. al., 1999		
4. Value established by researcher		
5. Assumption based on Anderson et. al., 1994		
6. Assumption based on Rittmann, 1993		
7. Headley et. al., 1998		

The biomass for this model will be proportioned in the same manner as it was in Model #2 except the biomass will be contained within the biofilm phase instead of the bulk aqueous phase. However, the total biomass for this model will equal the total biomass in the two pervious models.

Modeling Equations

For this model, two mass balance equations must be used, one for the bulk aqueous phase and one for the biofilm phase. Like Model #2, both Equations 3.3 and 3.4

will be applied in each sub-layer and the contaminant mass-flux out of one sub-layer is the contaminant mass-flux into the next sub-layer. Equation 3.3 is the mass balance equation for the bulk aqueous phase

$$\frac{dM}{dt} = QS_o - k_c A_{bio}\left(S_b - S_f\right) - QS_b \quad \textbf{(3.3)}$$

where S_b is the contaminant concentration in the bulk aqueous phase (M/L^3) and S_f is the contaminant concentration in the biofilm phase (M/L^3). The first and last terms in Equation 3.3 represents the mass-flux of contaminant into and out of the bulk aqueous phase, respectively. Contaminant mass-flux out of the bulk aqueous phase and into the biofilm phase, due to molecular diffusion through the stagnant liquid layer, is represented by the second term in Equation 3.3. The biofilm mass-flux term includes the mass transfer coefficient, k_c (L/T), and the biofilm surface area, A_{bio} (L^2).

Once the contaminant is in the biofilm, its biodegradation is governed by Monod kinetics. Additionally, the production of daughter products is calculated using the same conversion factors presented in Models #1 and #2. Once produced, the daughter product can either undergo further degradation within the biofilm or diffuse back into the bulk aqueous phase via the same mass transfer process explained in Equation 3.3.

Equation 3.4 is the mass balance equation used to define the mass-flux of contaminants within the biofilm.

$$\frac{dM_2}{dt} = k_{c2} A_{bio}(S_{b2} - S_{f2}) - \frac{k_2 X_{f2} S_{f2}}{K_{s2} + S_{f2}} + f_1 \frac{k_1 X_{f1} S_{f1}}{K_{s1} + S_{f1}} \quad \textbf{(3.4)}$$

The first term in Equation 3.4 represents the mass-flux of contaminant into and out of the biofilm. A positive difference between the bulk aqueous phase concentration,

S_b, and the biofilm phase concentration, S_f, will result in a mass-flux of compound #2 into the biofilm; whereas, a negative value will result in a mass-flux of compound #2 out of the biofilm.

The second term in Equation 3.4 represents the biodegradation of compound #2 via a Monod kinetic relationship and the third term represents the bioproduction of compound #2 due to the biodegradation of compound #1. An example relative to a system used to remediate chlorinated ethenes, would be PCE degrading within the biofilm to produce TCE.

Notice that Equation 3.4 does not contain a convective flux term like Equation 3.3. As stated in the assumptions for this model, longitudinal dispersion, diffusion, and convection within the biofilm will not be modeled. In order for a contaminant within the biofilm to move from one sub-layer to the next, it needs to first diffuse out of the biofilm into the bulk aqueous phase where it can then be transported via bulk convection.

.

Model Structure

Figure 3.7 shows the STELLA structure of Model #3

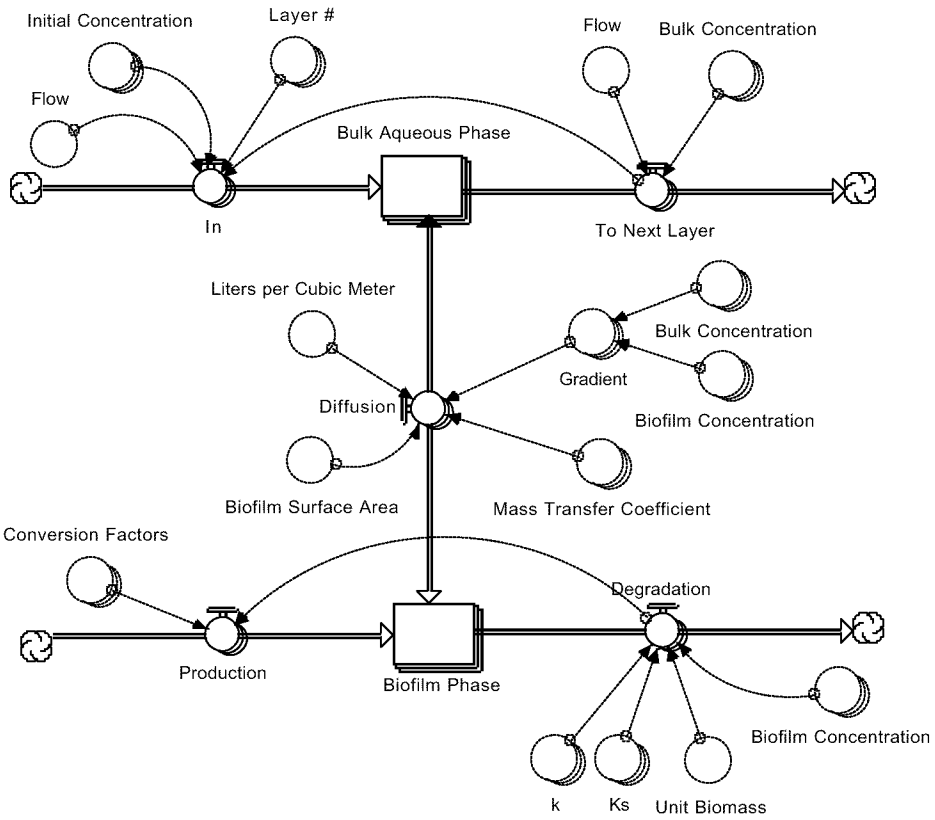


Figure 3.7. STELLA Structure of Model #3.

Notice that the degradation and production of contaminants only takes place in the biofilm phase and convection of contaminants takes place in the bulk aqueous phase. This model structure is congruent with our modeling assumptions stated above.

Testing

Validating a system dynamics model means to gain confidence in its ability to predict the behavior of the system. Testing the model is one way of gaining confidence. Two major categories of tests that can be conducted to validate a model are tests of model

structure and behavior. Tests of model structure include structure-verification and parameter-verification. These tests assess the structure of the model independently of the behavior. Tests of model behavior evaluate adequacy of model structure through analysis of behavior generated by the structure (Forrester and Senge, 1980). The model behavior test that most applies for this model is the behavior-reproduction test.

Implementation

Once there is confidence in the model, various simulations can be run to analyze the system and its behavior under varying conditions. Simulation data is presented and discussed in Chapter 4. Ideally, this model will provide insight into the effect that biofilm mass transfer processes and spatially varying contaminant concentrations have on constructed wetland contaminant effluent concentrations. Aspects from the models presented here and other models previously developed could be incorporated into an all-encompassing model. This model would prove to be a powerful management tool used in the design, assessment, and optimization of remediation wetlands with varying site conditions.

IV. Results and Discussion

Introduction

This chapter will compare and discuss the results obtained from three different modeling approaches describing the removal of chlorinated ethenes from a constructed wetland environment by microbial consortia. As discussed earlier, Model #1 describes the whole anaerobic region as a CSTR with the microorganisms suspended in the bulk aqueous phase. Model #2 discretizes Model #1 into several continuously stirred sub-layers that feed one-another much like a tanks-in-series system. The third model, Model #3, retains the discretization of Model #2 but incorporates a biofilm phase into which the contaminants must diffuse before they can be degraded.

Before any simulations are run and data are collected, it is important to structurally verify the models as designed in Chapter III. This can be done using structural tests used by System Dynamists when verifying models similar to the ones presented in Chapter III. The two most applicable structural tests that may be applied to this research are the structure-verification test and the parameter verification test.

Structure-Verification Test

This test assesses the structure of the model by directly comparing it to the structure of the real system. To pass the structure-verification test, the model structure must not contradict knowledge about the structure of the real system (Forrester and Senge, 1980).

Model #1

Comparing Model #1 to the real system, it becomes apparent why this research is being conducted. The CSTR model does not seem to mimic the real system at all.

Although the real system contains a large region in which water flows through and biodegradation occurs, the real system also has a spatial variability associated with it that the CSTR model does not. Contaminant, microorganism, and substrate concentrations all vary spatially through the wetland.

Even though Model #1 does not match the real system, it will still be used, as it is the baseline modeling approach to which the other models will be compared.

Model #2

Model #2 does a better job at mimicking reality because it incorporates a spatial component that attempts to account for and simulate the spatial variability of the real system. Discretizing the system into many sub-layers is an effort at capturing the effect of a spatially varying contaminant concentration. Other aspects of the model seem to be congruent with the real system as both the model and real system have a bulk aqueous phase in which biodegradation takes place.

While probably not the most ideal model, Model #2 does seem to incorporate the major aspects of the real system. Confidence in the model is increased when comparing Model #2 to Model #1.

Model #3

When compared to the real system, Model #3 seems to be logically structured. One can visualize the bulk aqueous and biofilm phases in the actual system just like the one represented in the biofilm model. The bulk aqueous phase in the real system would be the water that exists in the voids of the wetland soil. Similarly, the biofilm compartment would be the actual biofilm that exists on the soil particles. Additionally, the modeled flows can also be seen in the real system. The bulk flow into, through, and

out of the anaerobic layer of the actual system can be easily visualized because water is physically pumped into and drained out of the wetland.

Current knowledge of mass transfer in aquatic systems tells us that the transfer of solubilized compounds is governed both by a mass transfer coefficient and the gradient that exists between the compartments of the system. The biofilm model uses this knowledge to model the transfer of contaminants into and out of the biofilm phase.

Additionally, current research (Rittmann and McCarty, 1978, 1980, 1981; Suidan and Wang, 1985; Wang, Suidan, and Rittmann, 1986; Saez and Rittmann, 1987; Dykaar and Kitanidis, 1996; Polprasert et. al., 1998; MacDonald et. al., 1999) indicates that the degradation and production of contaminants like PCE, TCE, DCE, and VC take place predominantly in biofilms and that these reactions are governed by Monod kinetics. Taking these observations into account, confidence in the biofilm model is gained given that its structure mimics the structure of the real system.

Parameter-Verification Test

This test compares model parameter values with parameter values of the real system. Confidence is gained when model parameters conceptually and numerically correspond to knowledge of the real system (Forrester and Senge, 1980).

Several parameter values are used in the models presented in Chapter III. Water flow and initial PCE concentration are two input parameters used in the model. Both of these parameters are consistent with the corresponding values obtained from the wetland test cells at Wright-Patterson AFB, OH. Other parameters include the mass transfer coefficient and the Monod kinetic parameter values. The value of all these parameters have been either calculated using methods found in the literature or taken directly from

the literature. In some cases, parameter values were assumed or calculated based on certain assumptions. These assumptions were based on current literature and represent typical values found in wetland systems such as the one being modeled. Based on this analysis of the model parameters, confidence in the model parameters is gained.

Establishing the Reference Mode

Now that some level of confidence has been gained in the models through the structural tests performed above, the ability of the models to simulate the reference mode presented in Chapter III must be illustrated. The reference mode behavior shown in Figure 3.1 is reiterated below.

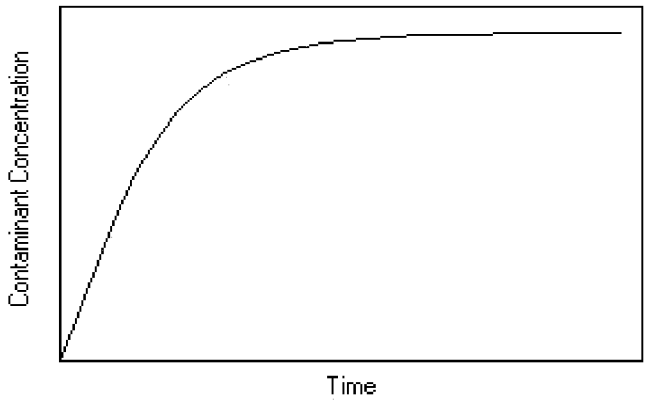


Figure 3.1. Reference Mode. Approach to Steady-State.

As the contaminant flows into the uncontaminated anaerobic region, the contaminant concentration will steadily increase. Convective flow and biodegradation will remove contaminant from the region simultaneously, gradually slowing down the increasing contaminant concentration until a steady-state condition is reached. This condition exists when the amount of contaminant coming into the region equals the

amount of contaminant leaving the region due to convective flow and biodegradation. Figures 4.1 thru 4.3 show the simulated behavior of all three models.

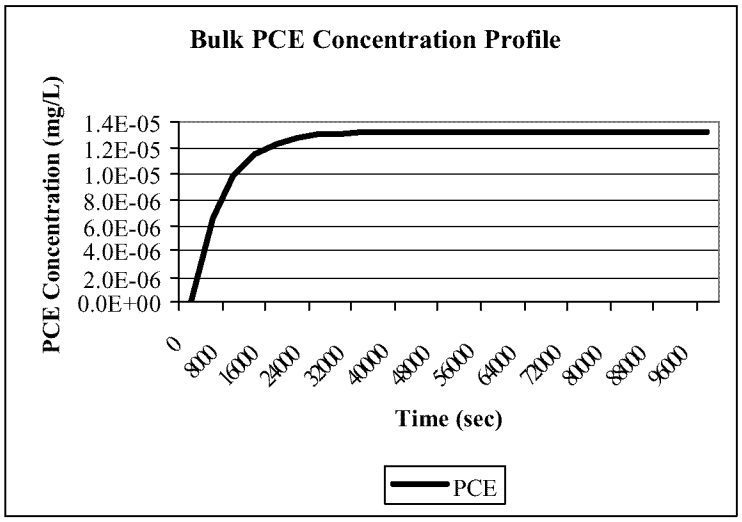


Figure 4.1. Model #1 simulated reference mode for bulk PCE.

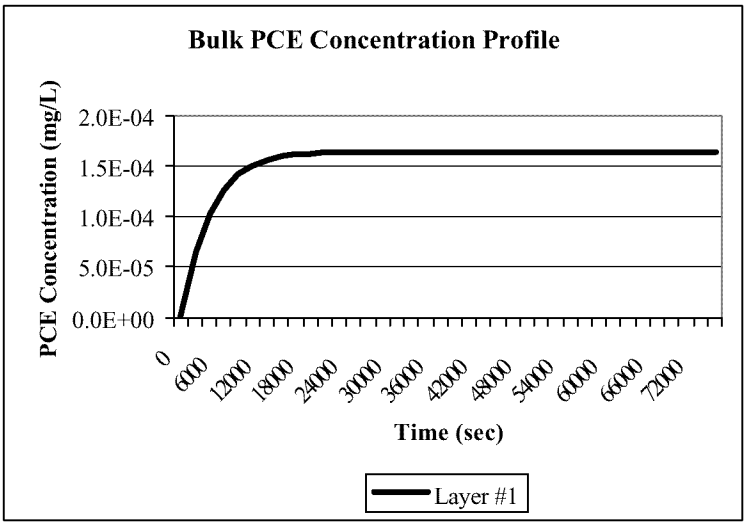


Figure 4.2. Model #2 simulated reference mode for bulk PCE.

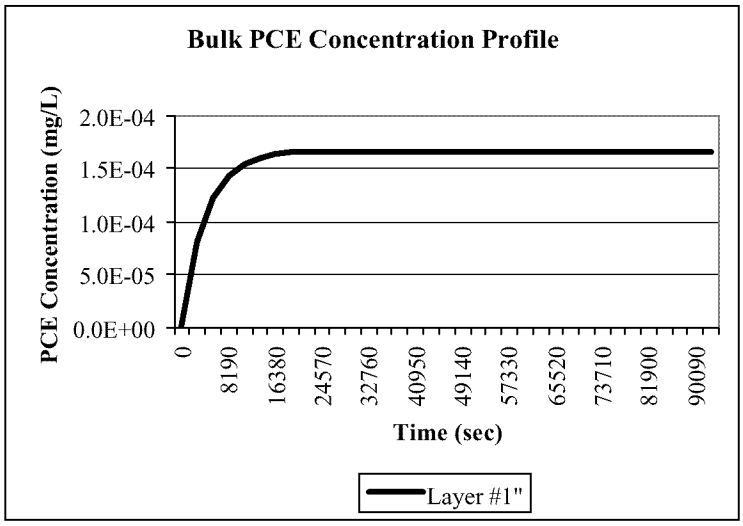


Figure 4.3. Model #3 simulated reference mode for bulk PCE.

Note that all of the models approach steady-state behavior in the manner predicted by the reference mode. Graphs depicting the approach to steady-state behavior for each contaminant, like the ones shown for PCE in Figures 4.1 thru 4.3, can be produced for all three models.

Considering that Model #1 has only one layer; only one graph, such as the one shown in Figure 4.1, can be constructed for each contaminant. On the other hand, Models #2 and #3 are multi-layer models and will have graphs like the ones shown in Figures 4.2 and 4.3 for all five contaminants in each layer.

Behavior-Reproduction Test

This test assesses how well the model behavior compares to the reference mode behavior, which is derived from a conceptual notion of how the real system would behave. Since model behavior is determined by its internal structure, changing parameter values outside the boundary of the model structure should not change the model behavior pattern.

This concept is illustrated in Figures 4.1 thru 4.3. With each model some sort of parameter outside of the model structure was changed without changing the overall system behavior. For instance, when Model #1 was discretized from one large layer into many sub-layers, the system behaved in the same manner as when there was just one layer. Similarly, when Model #2 was modified to incorporate diffusional processes, the system behavior remained unchanged.

While modifications to the models did affect contaminant effluent concentrations, as will be demonstrated later, the system behavior remained constant. This is evidence that the model structure is dictating the behavior of the model and not some random parameter.

Effluent Concentration Comparison

Previous modeling efforts by Hoefar and Roberts have used a CSTR assumption to model the flow and biodegradation of chlorinated ethenes in a constructed wetland environment. Model #1 mimics these modeling efforts and represents the baseline in this model comparison. Simulation data were collected for each model and the temporal and, in some cases, spatial change in contaminant concentrations were reported. Each model was run until all contaminant concentration levels reached a steady-state condition as depicted in Figures 4.1 thru 4.3. To compare the models, the steady-state effluent contaminant concentrations for each model were collected and are reported in Table 4.1 and Figure 4.4.

Table 4.1. Contaminant Effluent Concentrations (mg/L).

	PCE	TCE	DCE	VC	Ethene
Model #1	1.327×10^{-5}	6.204×10^{-6}	4.504×10^{-6}	1.593×10^{-4}	8.137×10^{-6}
Model #2	1.034×10^{-12}	1.226×10^{-12}	2.244×10^{-12}	1.693×10^{-4}	8.546×10^{-6}
Model #3	1.275×10^{-12}	1.506×10^{-12}	2.735×10^{-12}	1.689×10^{-4}	8.507×10^{-6}

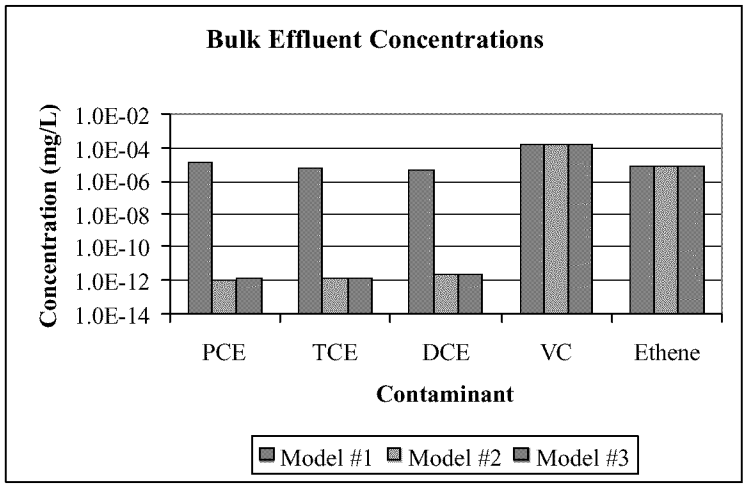


Figure 4.4. Graphical depiction of contaminant effluent concentrations for each model.

Looking at the data presented in Table 4.1 and Figure 4.4, note that Model #2, which incorporates a spatially varying contaminant concentration, results in PCE, TCE, and DCE effluent concentrations that are several orders of magnitude lower then the effluent concentrations obtained in Model #1. Given that the degradation kinetics of Models #1 and #2 are the same and that the only difference between the models is the discretization of Model #2 into eighteen sub-layers, the data suggests that a spatially varying contaminant concentration has a relatively significant effect on contaminant effluent concentrations. This observation follows intuition as discussed earlier.

Additionally, all of the contaminant effluent concentrations for Models #2 and #3 are of the same magnitude. Model #3 was similar to Model #2 except that it incorporated the biofilm concept. Since the data for the two models are so similar, it seems the biofilm concept holds little significance when simulating the removal of chlorinated ethenes in a constructed wetland. One explaination for the similarity of results between Models #2 and #3 might be that the characteristic diffusion time scale of the contaminants into the biofilm is shorter than the characteristic reaction time scale of the contaminants within the biofilm. That is, the biodegradation of the contaminants within the biofilm takes longer then the diffusion of contaminants into the biofilm, resulting in a system that is governed by the biodegradation kinetics and is thus reaction limited. An in-depth analysis and discussion of characteristic time scales will be conducted later in this chapter.

Another point of interest is the similarity between the VC and ethene effluent concentrations produced by Models #1, #2, and #3. A possible explanation for all three models producing similar VC and ethene concentrations is a time lag introduced into the system by the degradation process.

Analysis of Models #2 and #3

As noted above, all of the effluent concentrations for Models #2 and #3 are roughly of the same magnitude. After further investigation, not only are the effluent concentrations the same, but so are all the steady-state contaminant concentrations for each layer. That is, the spatial concentration profiles for all five contaminants are approximately similar for Models #2 and #3. Figures 4.5 thru 4.9 show the contaminant spatial profiles for Models #2 and #3.

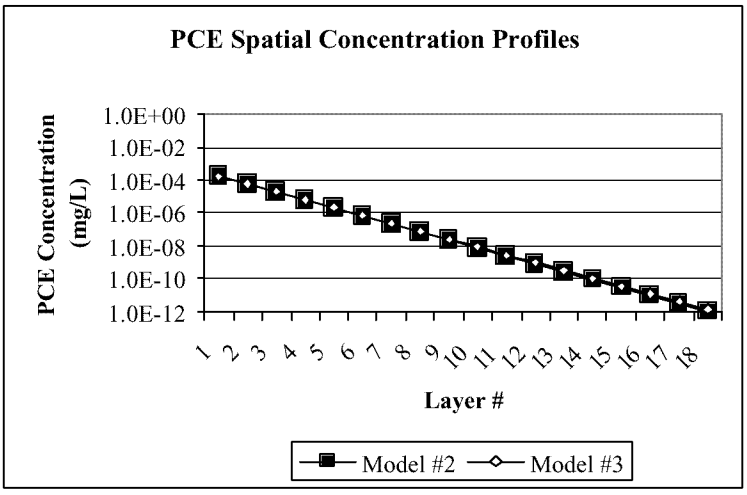


Figure 4.5. Bulk PCE spatial concentration profiles for Models #2 and #3.

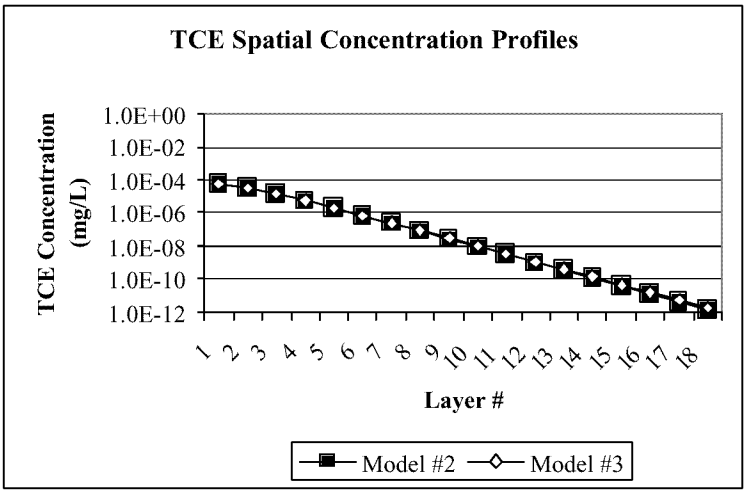


Figure 4.6. Bulk TCE spatial concentration profiles for Models #2 and #3.

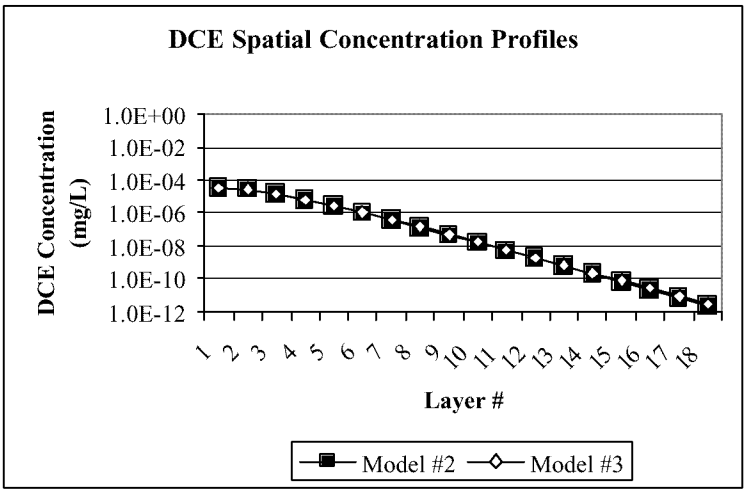


Figure 4.7. Bulk DCE spatial concentration profiles for Models #2 and #3.

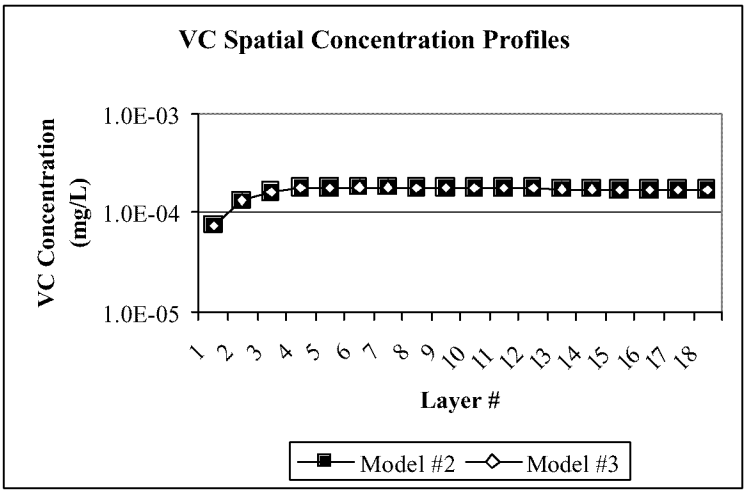


Figure 4.8. Bulk VC spatial concentration profiles for Models #2 and #3.

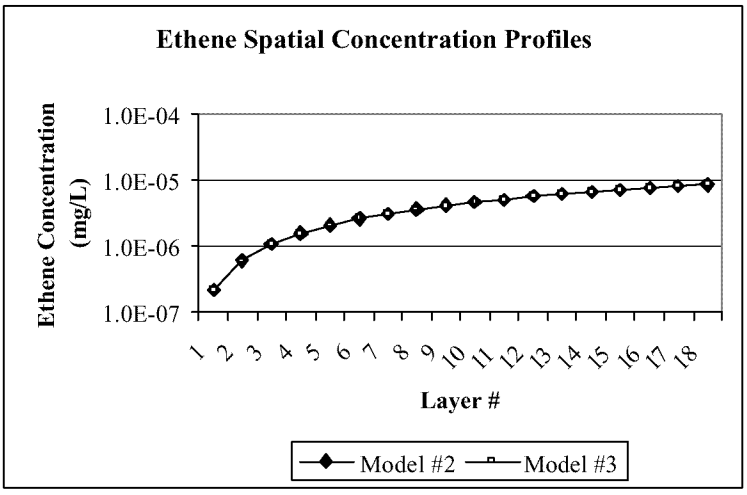


Figure 4.9. Bulk Ethene spatial concentration profiles for Models #2 and #3.

Notice that in Figures 4.5 thru 4.9, all of the data points from Model #3 appear to match the data points from Model #2. Without further investigation, it appears that the biofilm concept as modeled in Model #3 has little input on the final steady-state contaminant concentrations in each layer. However, when the effluent contaminant concentrations are compared through mathematical analysis, it becomes apparent that the biofilm concept as modeled in Model #3 does have an effect on effluent concentrations.

Mathematically comparing the PCE effluent concentrations from each model to one another reveals that the PCE effluent concentration simulated by Model #3 is 1.54 times greater than that of the PCE effluent concentration simulated by Model #2. This translates to a 54% increase in PCE effluent concentration from Model #2 to Model #3. This difference may seem insignificant at the low initial PCE concentration level these models are simulating, but the models are expected to behave in the same manner no matter what the initial PCE concentration. At higher initial PCE concentrations, a 54% increase could mean the difference between compliance and non-compliance with EPA

standards. Additionally, at higher initial PCE concentrations, the effect of the biofilm mechanism might become more apparent.

As stated earlier, one reason for the similarity between the two models could be explained by examining the characteristic time scales of both the reaction and the mass transfer process. Time scale analysis is used extensively throughout the engineering disciplines to help explain the relative importance of certain processes. Clark (1996) defines the characteristic time scale for an irreversible first-order reaction, τ_{rxn}, as being the inverse of the first-order reaction constant, k_{1st} (T^{-1}).

$$\tau_{rxn} = \frac{1}{k_{1st}} \quad \text{.....(4.1)}$$

Since the models are using Monod kinetics to describe the biodegradation of contaminants, a first-order reaction constant must be approximated using the Monod kinetic parameters. Fortunately, the contaminant concentrations simulated in the models are significantly lower than the contaminant half-saturation constants, K_s (M/L^3), used in the Monod equation. Since biomass is being held constant and contaminant concentrations are small relative to K_s, a first-order model can be used to approximate biodegradation kinetics (Charbeneau, 2000). After calculating the first-order reaction constant, it is determined that the characteristic reaction time for PCE is 16.4 seconds (see Appendix G for calculations). This means that it takes 16.4 seconds for one mole of PCE to degrade to e^{-1} moles of TCE.

Just as the characteristic time scale for the degradation reaction was calculated, so can the characteristic time scale for mass transfer be calculated. The mass transfer coefficient describes the rate at which a contaminant, like PCE, can be transported in a

particular environment. When forming the conceptual model of the biofilm system, a stagnant liquid layer resided between the bulk aqueous and biofilm phases. This stagnant liquid layer has a thickness that can be calculated in accordance with Equation 2.3 and is the distance over which the contaminant must travel in order to diffuse into the biofilm. Using the mass transfer coefficient, k_c (L/T), and the distance the contaminant must travel, L (L), the characteristic mass transport time scale can be calculated by dividing the stagnant liquid layer thickness by the mass transfer coefficient.

$$\tau_{trans} = \frac{L}{k_c} \qquad \textbf{(4.2)}$$

Using Equation 4.2, the characteristic mass transfer time scale for PCE has been calculated to be 82.4 seconds (see Appendix G for calculations). Comparing the reaction time scale to the mass transfer time scale, it is obvious that the mass transfer process takes longer then the reaction process. This means that the system is mass transfer limited. This conclusion further reinforces the notion that the biofilm concept has a significant effect on effluent concentrations.

The mathematical analysis of PCE effluent concentrations and characteristic time scales prompted further analysis into the effect of the mass transfer coefficient on effluent concentrations. Additional simulations were run to see what effect increasing and decreasing the mass transfer coefficient had on PCE effluent concentrations. Figure 4.10 shows the results of those simulations.

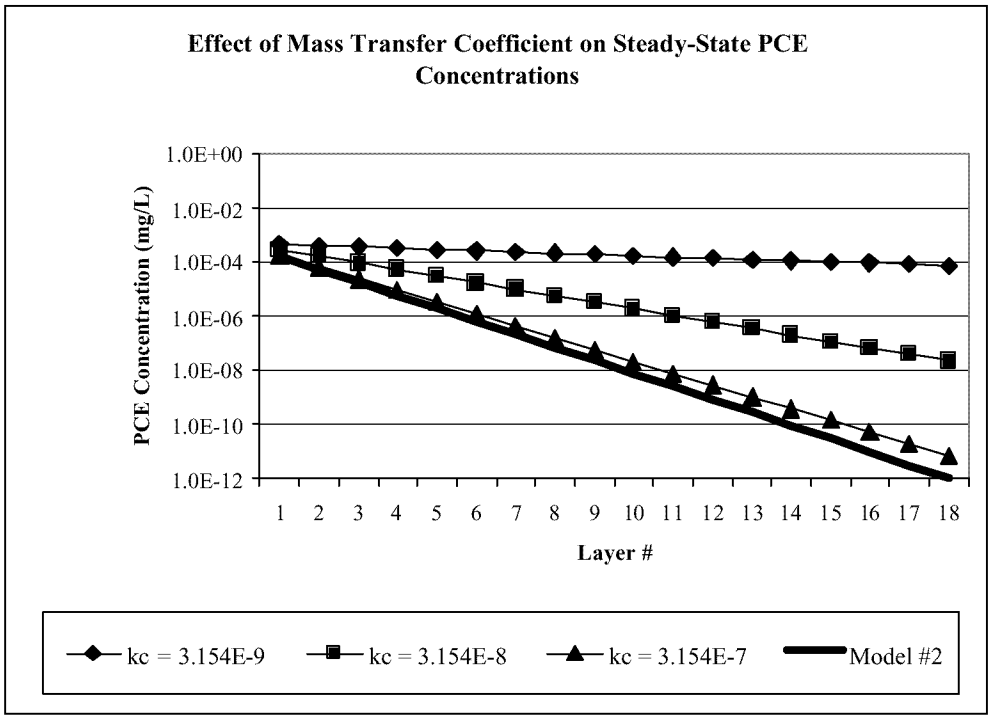


Figure 4.10. Spatial PCE concentration profiles of Model #3 with varying mass transfer coefficients, k_c.

Looking at Figure 4.10, it becomes apparent that as the mass transfer coefficient is increased, the spatial concentration profile approaches that of Model #2. This result is expected because as the mass transfer coefficient is increased, the rate at which the contaminant is transported into the biofilm is increased, resulting in higher biodegradation rates and lower bulk aqueous phase contaminant concentrations. Additionally, Model #2 represents the ideal case in which the contaminant is highly bioavailable due to the lack of a mass transfer limitation. So, it is expected that as the mass transfer coefficient is increased, its effect on limiting the bioavailability of the contaminant is decreased and the solution approaches that of Model #2.

When the mass transfer coefficient is low, the flow of contaminant into the biofilm is impeded, resulting in lower degradation rates and higher bulk aqueous phase

contaminant concentrations. If the mass transport coefficient is increased sufficiently, the spatial PCE concentration profile of Model #3 will match that of Model #2.

As shown above, contaminant effluent concentrations are dependent upon the mass transfer coefficient. The question of whether to use Model #2 or Model #3 when modeling the removal of chlorinated ethenes from a wetland environment can be answered by a simple calculation. Clark (1996) defines a term called the *second Damköhler number*, D_A^{II}, as the characteristic mass transfer time scale divided by the characteristic reaction time scale. This parameter is used to understand the limits of diffusion- and reaction-controlled mass transfer within the system.

$$D_A^{II} = \frac{\tau_{rxn}}{\tau_{trans}} \qquad \textbf{(4.3)}$$

Figure 4.11 demonstrates how diffusion and reaction lead to limits in mass transfer in problems where diffusion and reaction both come into play (Clark, 1996). The reaction-limited line represents a system where the mass transfer coefficient is very large, creating a situation where the reaction is limiting the amount of biodegradation. In addition to being comparable to Model #3 with a large mass transfer coefficient, this reaction-limited case is also comparable to Model #2, as there is no mass transfer mechanism to limit biodegradation; resulting in a system that is limited solely by reaction kinetics.

The diffusion-limited line in Figure 4.11 represents a system where the mass transfer coefficient is very small, resulting in a system where diffusion limits the amount of biodegradation. The diffusion-limited case is comparable to Model #3 with a very

small mass transfer coefficient that limits the amount of contaminant that diffuses into the biofilm for biodegradation.

The curved line on Figure 4.11 represents a system between the two extremes where both reaction and diffusion contribute to the mass transfer of contaminants. Notice that when D_A^{II} is greater then 10, the system is diffusion-limited. Conversely, when D_A^{II} is less then 10, the system approaches the reaction-limited state.

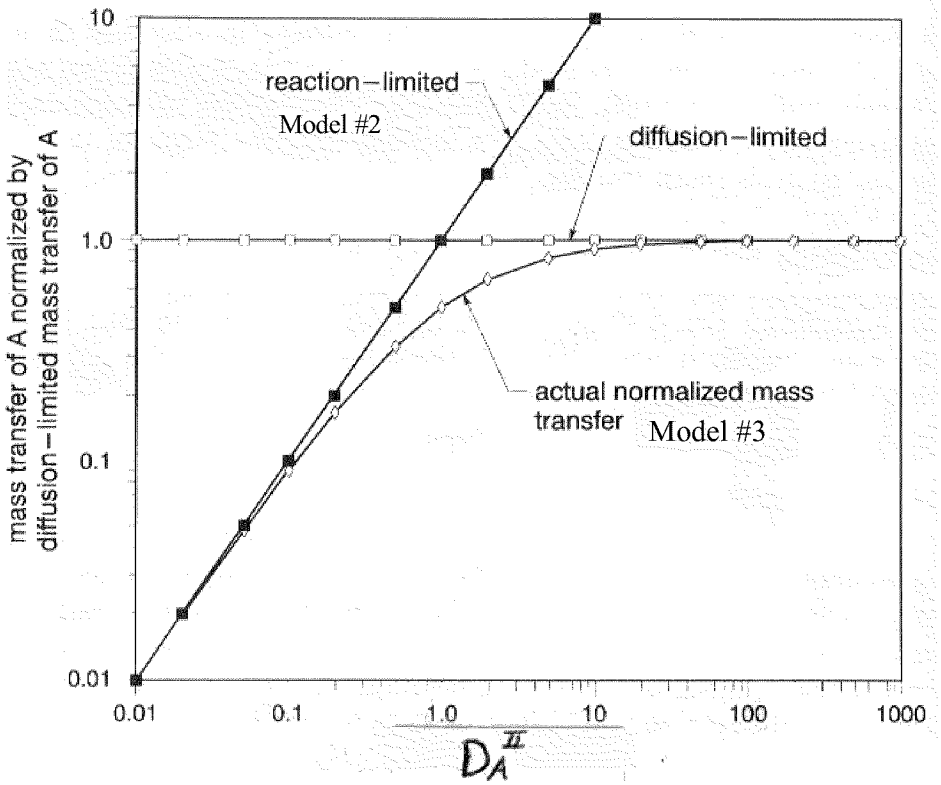


Figure 4.11. The relationship between the *second Damköhler number* and reaction- and diffusion-limitations within systems where reaction and diffusion play a role in mass transfer (Clark, 1996).

To illustrate how the *second Damköhler number* can be used to determine whether the system is diffusion- or reaction-limited, the *second Damköhler numbers* for

the mass transfer coefficients used in Figure 4.10 were calculated and reported in Table 4.2 below (see Appendix H for calculations). Notice that the *second Damköhler number* increases as the mass transfer coefficient decreases.

Table 4.2. S*econd Damköhler numbers* with varying mass transfer coefficients, k_c.

k_c (m/sec)	D_A^{II}
3.154E-05	1.579
3.154E-06	5.015
3.154E-07	15.786
3.154E-08	49.92
3.154E-09	157.861

As a general rule, if the *second Damköhler number* is greater than 10, the system is diffusion-limited and Model #3 can be used to approximate the removal of chlorinated ethenes from the system. Conversely, when the *second Damköhler number* is equal to or less than 10, Model #2 closely approximates the removal of contaminants from the system and may be used to simplify the problem. Within the system as defined in this research and all other things being held equal, the biodegradation of contaminants with mass transfer coefficients on the order of 10^{-6} or larger, could be approximated using Model #2. Conversely, contaminants with mass transfer coefficients less than 10^{-6} could be modeled using Model #3.

Model Verification

An equation developed in Clark (1996) can be used to verify that Models #1 and #2 are working properly. Equation 4.4 solves for the effluent concentration of a contaminant with a given influent concentration, C_{in} (M/L^3), and a given number of tanks

in series, N. For Model #1, the number of tanks, N, is equal to one and for Model #2, N is equal to 18.

$$C_{out} = \frac{C_{in}}{\left(1 + \frac{k_{1st} t_{bar}}{N}\right)^N} \quad \text{.....(4.4)}$$

Here, the approximated first order reaction constant, k_{1st} (T^{-1}), is used again in addition to the mean residence time, t_{bar} (T). Table 4.3 lists the PCE effluent concentrations for Models #1 and #2 using Equation 4.4 (see Appendix I for calculations). Note that the concentration reported for Models #1 and #2 in Table 4.3 match the concentrations for 1 and 18 tanks reported in Table 4.1, respectively. This is evidence that Models #1 and #2 are constructed correctly and produce valid simulation results.

Table 4.3. PCE Effluent Concentrations Calculated using Equation 4.4.

	PCE Effluent Concentration (mg/L)
1 Tank	1.327×10^{-5}
18 Tanks	1.032×10^{-12}

V. Conclusions and Recommendations

The purpose of this research was to investigate alternate approaches to modeling the removal of chlorinated ethenes from groundwater within a constructed wetland. Three different modeling approaches were developed and evaluated. A mechanistic approach was used in this research that investigated the internal structure of the system and the behavior resulting from that structure.

Conclusions

This research revealed that a spatially varying contaminant concentration, modeled by both Models #2 and #3, has a profound effect on contaminant effluent concentrations. It is conceivable that a spatially varying contaminant concentration, when incorporated into a more complex model, will affect not only effluent concentrations, but biomass growth and the removal of other growth substrates, as well. Modeling the regions of a constructed wetland as a CSTR seems to underestimate the removal of chlorinated ethenes when compared to the tanks-in-series or biofilm modeling approaches. Methods developed in this research are simple and can easily be incorporated into previously developed models, adding more detail and perhaps a better representation of the actual system.

Additionally, the incorporation of a biofilm concept revealed that a mass transfer process could have a limiting effect on biodegradation in a constructed wetland. Model #3 illustrated that depending on the kinetics of biodegradation and mass transfer, a biofilm concept can greatly affect contaminant effluent concentrations.

Model Limitations

As in any model analysis, assumptions about the system were made and resulted in some model limitations in describing reality. One such limitation is that biomass growth was not modeled in any of the models developed in this research. Just as contaminant concentration levels are significant when determining the amount of contaminant that undergoes biodegradation, the amount of biomass available to perform biodegradation is important as well. All of the models assumed a constant biomass concentration throughout the constructed wetland. This assumption aided in controlling the experiment so that model simulation results could be compared and differences between simulation results could not be attributed to varying levels of biomass.

In addition to a constant biomass concentration, the models also assumed a very simplistic microbial population dynamic. It was assumed that four distinct microbial populations governed over the biodegradation of the chlorinated ethenes in the system, each population capable of only degrading one of the four contaminants (PCE, TCE, DCE, VC). This approach was taken to simplify the system; however, it neglects more complex microbial populations that can degrade multiple contaminants or can degrade contaminants from one form to a lower form, skipping intermediate forms.

Another limitation of the model imposed by initial assumptions was that biodegradation occurred at any level of contaminant concentration. In the literature, researchers (Rittmann and McCarty, 1980, 1981; Saez and Rittmann, 1988; Rittmann, 1993) introduce the concept of a minimum contaminant concentration below which no biomass activity occurs. That is, there is a minimum contaminant concentration that is

required to sustain certain types of microbial populations and that without these minimum concentrations, the microbial population will no longer thrive.

Additionally, competition was not modeled to simplify the experiment and to focus on the main objective of the research. Like the minimum contaminant concentration concept, competition for electron donors and acceptors among microbial populations could have a significant effect on the biodegradation of chlorinated ethenes in a constructed wetland.

Incorporating the concepts of biomass growth, complex microbial population dynamics, minimum sustainable contaminant concentration, and competition into the model would further add detail and realism to the models presented in this study.

Recommendations for Further Study

1. Incorporate a spatially varying contaminant concentration into a model that simulates processes such as; biomass growth, complex microbial population dynamic, minimum sustainable contaminant concentration, and competition.

2. Further investigate the biofilm concept by exploring possible analytical solutions that describe the mass transfer of contaminants into a biofilm where biodegradation occurs. These solutions would eliminate the need to model the biofilm as a CSTR and consider a contaminant concentration profile within the biofilm when determining the mass flux of contaminant into the biofilm.

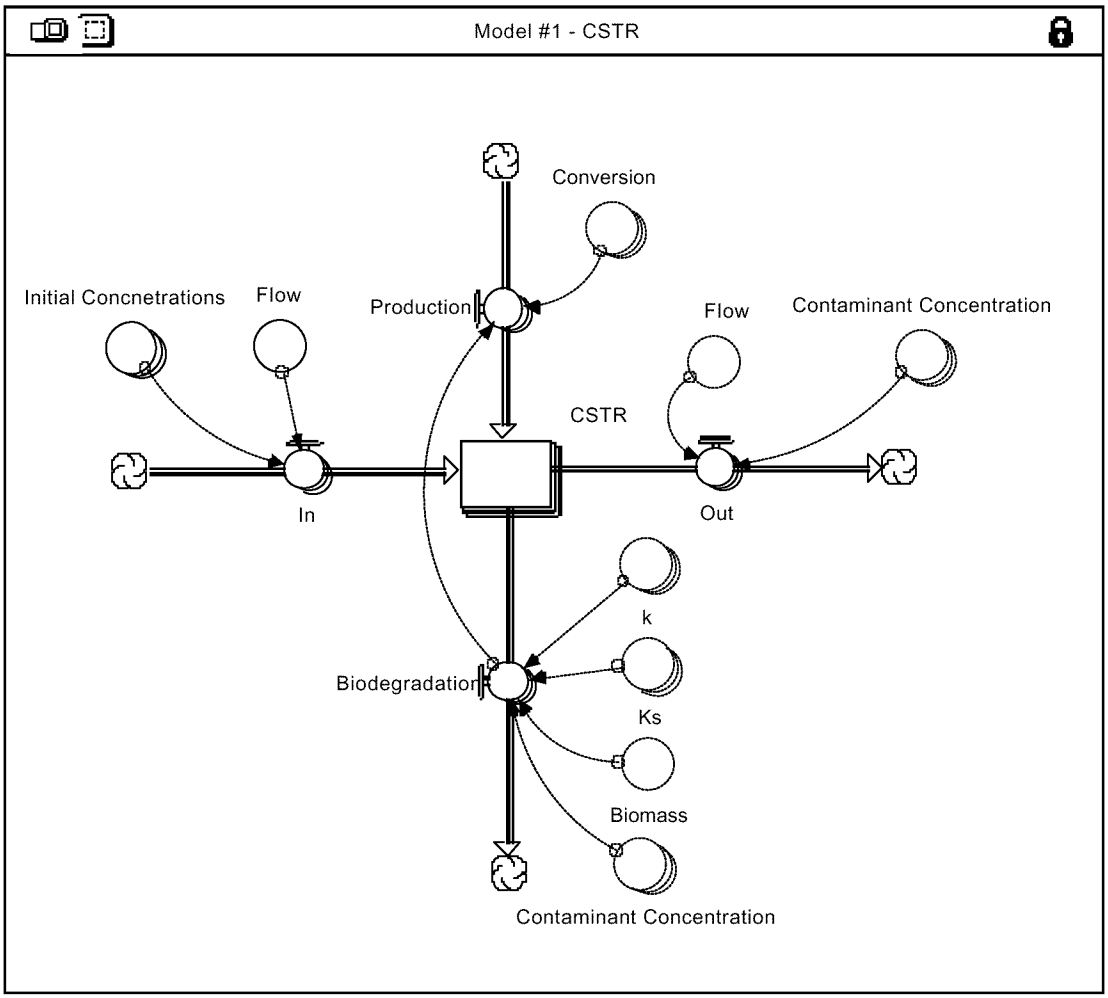
3. Currently, there is limited information on Monod kinetic and mass transfer parameters associated with constructed wetlands used for the remediation of chlorinated ethenes. Further research into the values of the maximum substrate utilization rate, k (T^{-1}), the half saturation constant, K_m (M/L^3), and the mass transfer coefficient, k_c (L/T), for chlorinated ethenes in a constructed wetland environment would add great detail and value to any future modeling efforts.

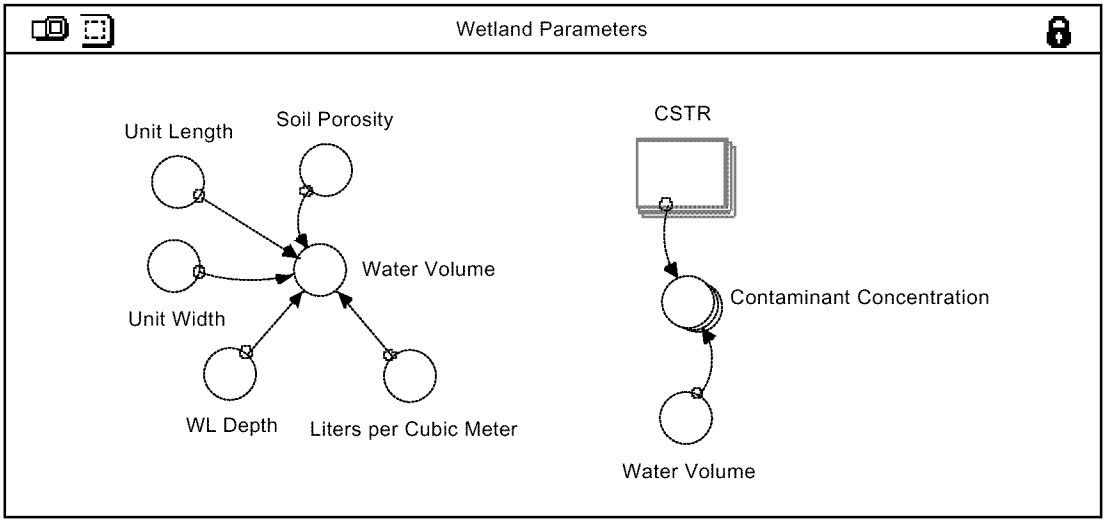
Final Assessment of the Thesis Effort

Wetland environments are complex and dynamic systems that include many interrelating processes. The use of mechanistic models is an excellent way to investigate and understand the intricacies of these complex systems. Through the development and application of models, one may begin to understand the processes and structure that affect system behavior.

Further development of mechanistic models that simulate the processes and interactions within constructed wetland environments will contribute to knowledge about these systems. Environmental managers and design engineers could then use this knowledge to manage, design and optimize constructed wetlands for the use of chlorinated ethene remediation. Use of constructed wetlands for remediation purposes could provide to be a viable alternative to current methods and prove to be more cost effective and environmentally friendly.

Appendix A – Model #1 STELLA Structure





Appendix B – Model #1 Equations

Model #1 – CSTR:

Mass Balance:

CSTR[Contaminants](t) = Contaminant[Contaminants](t - dt) + (In[Contaminants]
+ Production[Contaminants] - Out[Contaminants] -
Biodegradation[Contaminants]) * dt
INIT CSTR[Contaminants] = 0

CSTR Inflows:

In[Contaminants] = Flow*Initial_Concentrations[Contaminants]
Production[PCE] = Biodegradation[Ethene]*Conversion[Ethene]
Production[TCE] = Biodegradation[PCE]*Conversion[PCE]
Production[DCE] = Biodegradation[TCE]*Conversion[TCE]
Production[VC] = Biodegradation[DCE]*Conversion[DCE]
Production[Ethene] = Biodegradation[VC]*Conversion[VC]

CSTR Outflows:

Out[Contaminants] = Flow*Contaminant_Con[Contaminants]
Biodegradation[Contaminants] =
(k[Contaminants]*Contaminant_Con[Contaminants]*Biomass)/(Ks[Contaminants
]+Contaminant_Con[Contaminants])

Parameters:

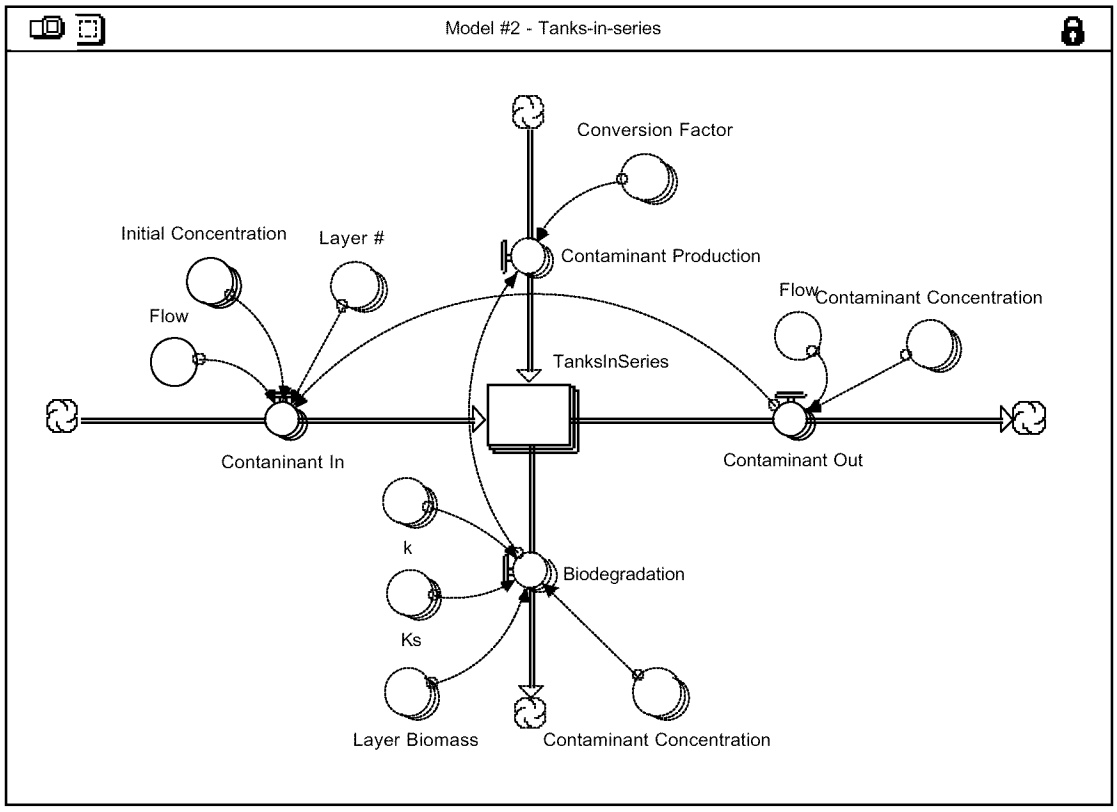
Biomass = 40.66
Contaminant_Concentration[Contaminants] =
Contaminant[Contaminants]/Water_Volume
Conversion[PCE] = .79222
Conversion[TCE] = .737724
Conversion[DCE] = .644479
Conversion[VC] = .448359
Conversion[Ethene] = 0
Flow = .001026
Initial_Concentrations[PCE] = .0005
Initial_Concentrations[TCE] = 0
Initial_Concentrations[DCE] = 0
Initial_Concentrations[VC] = 0
Initial_Concentrations[Ethene] = 0
k[PCE] = 8.292E-5
k[TCE] = 1.095E-4
k[DCE] = 8.075E-5
k[VC] = 5.21E-5
k[Ethene] = 0

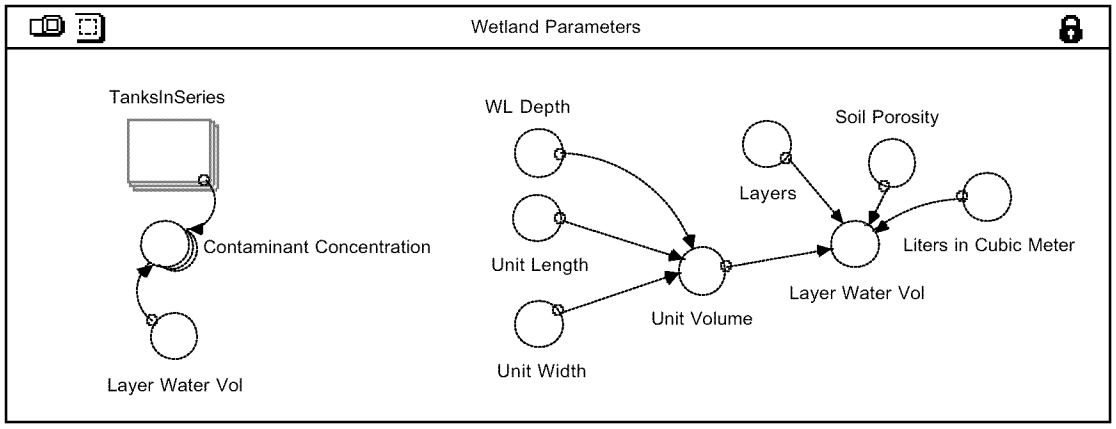
Ks[PCE] = .0896
Ks[TCE] = .07096
Ks[DCE] = .05233
Ks[VC] = 18.125
Ks[Ethene] = 1

Wetland Parameters:

Liters_per_Cubic_Meter = 1000
Soil_Porosity = .5
Unit_Length = 1
Unit_Width = 1
Water_Volume =
(Unit_Length*Unit_Width*WL_Depth)*Soil_Porosity*Liters_per_Cubic_Meter
WL_Depth = .4572

Appendix C – Model #2 STELLA Structure





Appendix D – Model #2 Equations

Model #2 - Tanks-in-series:

Mass Balance:

```
TanksInSeries[Layer_Number,Contaminant](t) =
        TanksInSeries[Layer_Number,Contaminant](t - dt) +
        (Contaminant_In[Layer_Number,Contaminant] +
        Contaminant_Production[Layer_Number,Contaminant] -
        Contaminant_Out[Layer_Number,Contaminant] -
        Biodegradation[Layer_Number,Contaminant]) * dt
INIT Layer[Layer_Number,Contaminant] = 0
```

Inflows:

```
Contaminant_In[1,PCE] = IF(Layer_#[1]=1)
        THEN(Initial_Concentration[PCE]*Flow)
        ELSE(Contaminant_Out[1,PCE])
Contaminant_In[1,TCE] = IF(Layer_#[1]=1)
        THEN(Initial_Concentration[TCE]*Flow)
        ELSE(Contaminant_Out[1,TCE])
Contaminant_In[1,DCE] = IF(Layer_#[1]=1)
        THEN(Initial_Concentration[DCE]*Flow)
        ELSE(Contaminant_Out[1,DCE])
Contaminant_In[1,VC] = IF(Layer_#[1]=1)
        THEN(Initial_Concentration[VC]*Flow)
        ELSE(Contaminant_Out[1,VC])
Contaminant_In[1,Ethene] = IF(Layer_#[1]=1)
        THEN(Initial_Concentration[Ethene]*Flow)
        ELSE(Contaminant_Out[1,Ethene])
Contaminant_In[2,PCE] = IF(Layer_#[2]=1)
        THEN(Initial_Concentration[PCE]*Flow)
        ELSE(Contaminant_Out[1,PCE])
Contaminant_In[2,TCE] = IF(Layer_#[2]=1)
        THEN(Initial_Concentration[TCE]*Flow)
        ELSE(Contaminant_Out[1,TCE])
Contaminant_In[2,DCE] = IF(Layer_#[2]=1)
        THEN(Initial_Concentration[DCE]*Flow)
        ELSE(Contaminant_Out[1,DCE])
Contaminant_In[2,VC] = IF(Layer_#[2]=1)
        THEN(Initial_Concentration[VC]*Flow)
        ELSE(Contaminant_Out[1,VC])
Contaminant_In[2,Ethene] = IF(Layer_#[2]=1)
        THEN(Initial_Concentration[Ethene]*Flow)
        ELSE(Contaminant_Out[1,Ethene])
```

```
Contaminant_In[3,PCE] = IF(Layer_#[3]=1)
        THEN(Initial_Concentration[PCE]*Flow)
        ELSE(Contaminant_Out[2,PCE])
Contaminant_In[3,TCE] = IF(Layer_#[3]=1)
        THEN(Initial_Concentration[TCE]*Flow)
        ELSE(Contaminant_Out[2,TCE])
Contaminant_In[3,DCE] = IF(Layer_#[3]=1)
        THEN(Initial_Concentration[DCE]*Flow)
        ELSE(Contaminant_Out[2,DCE])
Contaminant_In[3,VC] = IF(Layer_#[3]=1)
        THEN(Initial_Concentration[VC]*Flow)
        ELSE(Contaminant_Out[2,VC])
Contaminant_In[3,Ethene] = IF(Layer_#[3]=1)
        THEN(Initial_Concentration[Ethene]*Flow)
        ELSE(Contaminant_Out[2,Ethene])
Contaminant_In[4,PCE] = IF(Layer_#[4]=1)
        THEN(Initial_Concentration[PCE]*Flow)
        ELSE(Contaminant_Out[3,PCE])
Contaminant_In[4,TCE] = IF(Layer_#[4]=1)
        THEN(Initial_Concentration[TCE]*Flow)
        ELSE(Contaminant_Out[3,TCE])
Contaminant_In[4,DCE] = IF(Layer_#[4]=1)
        THEN(Initial_Concentration[DCE]*Flow)
        ELSE(Contaminant_Out[3,DCE])
Contaminant_In[4,VC] = IF(Layer_#[4]=1)
        THEN(Initial_Concentration[VC]*Flow)
        ELSE(Contaminant_Out[3,VC])
Contaminant_In[4,Ethene] = IF(Layer_#[4]=1)
        THEN(Initial_Concentration[Ethene]*Flow)
        ELSE(Contaminant_Out[3,Ethene])
Contaminant_In[5,PCE] = IF(Layer_#[5]=1)
        THEN(Initial_Concentration[PCE]*Flow)
        ELSE(Contaminant_Out[4,PCE])
Contaminant_In[5,TCE] = IF(Layer_#[5]=1)
        THEN(Initial_Concentration[TCE]*Flow)
        ELSE(Contaminant_Out[4,TCE])
Contaminant_In[5,DCE] = IF(Layer_#[5]=1)
        THEN(Initial_Concentration[DCE]*Flow)
        ELSE(Contaminant_Out[4,DCE])
Contaminant_In[5,VC] = IF(Layer_#[5]=1)
        THEN(Initial_Concentration[VC]*Flow)
        ELSE(Contaminant_Out[4,VC])
Contaminant_In[5,Ethene] = IF(Layer_#[5]=1)
        THEN(Initial_Concentration[Ethene]*Flow)
        ELSE(Contaminant_Out[4,Ethene])
```

```
Contaminant_In[6,PCE] = IF(Layer_#[6]=1)
        THEN(Initial_Concentration[PCE]*Flow)
        ELSE(Contaminant_Out[5,PCE])
Contaminant_In[6,TCE] = IF(Layer_#[6]=1)
        THEN(Initial_Concentration[TCE]*Flow)
        ELSE(Contaminant_Out[5,TCE])
Contaminant_In[6,DCE] = IF(Layer_#[6]=1)
        THEN(Initial_Concentration[DCE]*Flow)
        ELSE(Contaminant_Out[5,DCE])
Contaminant_In[6,VC] = IF(Layer_#[6]=1)
        THEN(Initial_Concentration[VC]*Flow)
        ELSE(Contaminant_Out[5,VC])
Contaminant_In[6,Ethene] = IF(Layer_#[6]=1)
        THEN(Initial_Concentration[Ethene]*Flow)
        ELSE(Contaminant_Out[5,Ethene])
Contaminant_In[7,PCE] = IF(Layer_#[7]=1)
        THEN(Initial_Concentration[PCE]*Flow)
        ELSE(Contaminant_Out[6,PCE])
Contaminant_In[7,TCE] = IF(Layer_#[7]=1)
        THEN(Initial_Concentration[TCE]*Flow)
        ELSE(Contaminant_Out[6,TCE])
Contaminant_In[7,DCE] = IF(Layer_#[7]=1)
        THEN(Initial_Concentration[DCE]*Flow)
        ELSE(Contaminant_Out[6,DCE])
Contaminant_In[7,VC] = IF(Layer_#[7]=1)
        THEN(Initial_Concentration[VC]*Flow)
        ELSE(Contaminant_Out[6,VC])
Contaminant_In[7,Ethene] = IF(Layer_#[7]=1)
        THEN(Initial_Concentration[Ethene]*Flow)
        ELSE(Contaminant_Out[6,Ethene])
Contaminant_In[8,PCE] = IF(Layer_#[8]=1)
        THEN(Initial_Concentration[PCE]*Flow)
        ELSE(Contaminant_Out[7,PCE])
Contaminant_In[8,TCE] = IF(Layer_#[8]=1)
        THEN(Initial_Concentration[TCE]*Flow)
        ELSE(Contaminant_Out[7,TCE])
Contaminant_In[8,DCE] = IF(Layer_#[8]=1)
        THEN(Initial_Concentration[DCE]*Flow)
        ELSE(Contaminant_Out[7,DCE])
Contaminant_In[8,VC] = IF(Layer_#[8]=1)
        THEN(Initial_Concentration[VC]*Flow)
        ELSE(Contaminant_Out[7,VC])
Contaminant_In[8,Ethene] = IF(Layer_#[8]=1)
        THEN(Initial_Concentration[Ethene]*Flow)
        ELSE(Contaminant_Out[7,Ethene])
```

```
Contaminant_In[9,PCE] = IF(Layer_#[9]=1)
        THEN(Initial_Concentration[PCE]*Flow)
        ELSE(Contaminant_Out[8,PCE])
Contaminant_In[9,TCE] = IF(Layer_#[9]=1)
        THEN(Initial_Concentration[TCE]*Flow)
        ELSE(Contaminant_Out[8,TCE])
Contaminant_In[9,DCE] = IF(Layer_#[9]=1)
        THEN(Initial_Concentration[DCE]*Flow)
        ELSE(Contaminant_Out[8,DCE])
Contaminant_In[9,VC] = IF(Layer_#[9]=1)
        THEN(Initial_Concentration[VC]*Flow)
        ELSE(Contaminant_Out[8,VC])
Contaminant_In[9,Ethene] = IF(Layer_#[9]=1)
        THEN(Initial_Concentration[Ethene]*Flow)
        ELSE(Contaminant_Out[8,Ethene])
Contaminant_In[10,PCE] = IF(Layer_#[10]=1)
        THEN(Initial_Concentration[PCE]*Flow)
        ELSE(Contaminant_Out[9,PCE])
Contaminant_In[10,TCE] = IF(Layer_#[10]=1)
        THEN(Initial_Concentration[TCE]*Flow)
        ELSE(Contaminant_Out[9,TCE])
Contaminant_In[10,DCE] = IF(Layer_#[10]=1)
        THEN(Initial_Concentration[DCE]*Flow)
        ELSE(Contaminant_Out[9,DCE])
Contaminant_In[10,VC] = IF(Layer_#[10]=1)
        THEN(Initial_Concentration[VC]*Flow)
        ELSE(Contaminant_Out[9,VC])
Contaminant_In[10,Ethene] = IF(Layer_#[10]=1)
        THEN(Initial_Concentration[Ethene]*Flow)
        ELSE(Contaminant_Out[9,Ethene])
Contaminant_In[11,PCE] = IF(Layer_#[11]=1)
        THEN(Initial_Concentration[PCE]*Flow)
        ELSE(Contaminant_Out[10,PCE])
Contaminant_In[11,TCE] = IF(Layer_#[11]=1)
        THEN(Initial_Concentration[TCE]*Flow)
        ELSE(Contaminant_Out[10,TCE])
Contaminant_In[11,DCE] = IF(Layer_#[11]=1)
        THEN(Initial_Concentration[DCE]*Flow)
        ELSE(Contaminant_Out[10,DCE])
Contaminant_In[11,VC] = IF(Layer_#[11]=1)
        THEN(Initial_Concentration[VC]*Flow)
        ELSE(Contaminant_Out[10,VC])
Contaminant_In[11,Ethene] = IF(Layer_#[11]=1)
        THEN(Initial_Concentration[Ethene]*Flow)
        ELSE(Contaminant_Out[10,Ethene])
```

```
Contaminant_In[12,PCE] = IF(Layer_#[12]=1)
        THEN(Initial_Concentration[PCE]*Flow)
        ELSE(Contaminant_Out[11,PCE])
Contaminant_In[12,TCE] = IF(Layer_#[12]=1)
        THEN(Initial_Concentration[TCE]*Flow)
        ELSE(Contaminant_Out[11,TCE])
Contaminant_In[12,DCE] = IF(Layer_#[12]=1)
        THEN(Initial_Concentration[DCE]*Flow)
        ELSE(Contaminant_Out[11,DCE])
Contaminant_In[12,VC] = IF(Layer_#[12]=1)
        THEN(Initial_Concentration[VC]*Flow)
        ELSE(Contaminant_Out[11,VC])
Contaminant_In[12,Ethene] = IF(Layer_#[12]=1)
        THEN(Initial_Concentration[Ethene]*Flow)
        ELSE(Contaminant_Out[11,Ethene])
Contaminant_In[13,PCE] = IF(Layer_#[13]=1)
        THEN(Initial_Concentration[PCE]*Flow)
        ELSE(Contaminant_Out[12,PCE])
Contaminant_In[13,TCE] = IF(Layer_#[13]=1)
        THEN(Initial_Concentration[TCE]*Flow)
        ELSE(Contaminant_Out[12,TCE])
Contaminant_In[13,DCE] = IF(Layer_#[13]=1)
        THEN(Initial_Concentration[DCE]*Flow)
        ELSE(Contaminant_Out[12,DCE])
Contaminant_In[13,VC] = IF(Layer_#[13]=1)
        THEN(Initial_Concentration[VC]*Flow)
        ELSE(Contaminant_Out[12,VC])
Contaminant_In[13,Ethene] = IF(Layer_#[13]=1)
        THEN(Initial_Concentration[Ethene]*Flow)
        ELSE(Contaminant_Out[12,Ethene])
Contaminant_In[14,PCE] = IF(Layer_#[14]=1)
        THEN(Initial_Concentration[PCE]*Flow)
        ELSE(Contaminant_Out[13,PCE])
Contaminant_In[14,TCE] = IF(Layer_#[14]=1)
        THEN(Initial_Concentration[TCE]*Flow)
        ELSE(Contaminant_Out[13,TCE])
Contaminant_In[14,DCE] = IF(Layer_#[14]=1)
        THEN(Initial_Concentration[DCE]*Flow)
        ELSE(Contaminant_Out[13,DCE])
Contaminant_In[14,VC] = IF(Layer_#[14]=1)
        THEN(Initial_Concentration[VC]*Flow)
        ELSE(Contaminant_Out[13,VC])
Contaminant_In[14,Ethene] = IF(Layer_#[14]=1)
        THEN(Initial_Concentration[Ethene]*Flow)
        ELSE(Contaminant_Out[13,Ethene])
```

```
Contaminant_In[15,PCE] = IF(Layer_#[15]=1)
        THEN(Initial_Concentration[PCE]*Flow)
        ELSE(Contaminant_Out[14,PCE])
Contaminant_In[15,TCE] = IF(Layer_#[15]=1)
        THEN(Initial_Concentration[TCE]*Flow)
        ELSE(Contaminant_Out[14,TCE])
Contaminant_In[15,DCE] = IF(Layer_#[15]=1)
        THEN(Initial_Concentration[DCE]*Flow)
        ELSE(Contaminant_Out[14,DCE])
Contaminant_In[15,VC] = IF(Layer_#[15]=1)
        THEN(Initial_Concentration[VC]*Flow)
        ELSE(Contaminant_Out[14,VC])
Contaminant_In[15,Ethene] = IF(Layer_#[15]=1)
        THEN(Initial_Concentration[Ethene]*Flow)
        ELSE(Contaminant_Out[14,Ethene])
Contaminant_In[16,PCE] = IF(Layer_#[16]=1)
        THEN(Initial_Concentration[PCE]*Flow)
        ELSE(Contaminant_Out[15,PCE])
Contaminant_In[16,TCE] = IF(Layer_#[16]=1)
        THEN(Initial_Concentration[TCE]*Flow)
        ELSE(Contaminant_Out[15,TCE])
Contaminant_In[16,DCE] = IF(Layer_#[16]=1)
        THEN(Initial_Concentration[DCE]*Flow)
        ELSE(Contaminant_Out[15,DCE])
Contaminant_In[16,VC] = IF(Layer_#[16]=1)
        THEN(Initial_Concentration[VC]*Flow)
        ELSE(Contaminant_Out[15,VC])
Contaminant_In[16,Ethene] = IF(Layer_#[16]=1)
        THEN(Initial_Concentration[Ethene]*Flow)
        ELSE(Contaminant_Out[15,Ethene])
Contaminant_In[17,PCE] = IF(Layer_#[17]=1)
        THEN(Initial_Concentration[PCE]*Flow)
        ELSE(Contaminant_Out[16,PCE])
Contaminant_In[17,TCE] = IF(Layer_#[17]=1)
        THEN(Initial_Concentration[TCE]*Flow)
        ELSE(Contaminant_Out[16,TCE])
Contaminant_In[17,DCE] = IF(Layer_#[17]=1)
        THEN(Initial_Concentration[DCE]*Flow)
        ELSE(Contaminant_Out[16,DCE])
Contaminant_In[17,VC] = IF(Layer_#[17]=1)
        THEN(Initial_Concentration[VC]*Flow)
        ELSE(Contaminant_Out[16,VC])
Contaminant_In[17,Ethene] = IF(Layer_#[17]=1)
        THEN(Initial_Concentration[Ethene]*Flow)
        ELSE(Contaminant_Out[16,Ethene])
```

```
Contaminant_In[18,PCE] = IF(Layer_#[18]=1)
        THEN(Initial_Concentration[PCE]*Flow)
        ELSE(Contaminant_Out[17,PCE])
Contaminant_In[18,TCE] = IF(Layer_#[18]=1)
        THEN(Initial_Concentration[TCE]*Flow)
        ELSE(Contaminant_Out[17,TCE])
Contaminant_In[18,DCE] = IF(Layer_#[18]=1)
        THEN(Initial_Concentration[DCE]*Flow)
        ELSE(Contaminant_Out[17,DCE])
Contaminant_In[18,VC] = IF(Layer_#[18]=1)
        THEN(Initial_Concentration[VC]*Flow)
        ELSE(Contaminant_Out[17,VC])
Contaminant_In[18,Ethene] = IF(Layer_#[18]=1)
        THEN(Initial_Concentration[Ethene]*Flow)
        ELSE(Contaminant_Out[17,Ethene])
Contaminant_Production[1,PCE] = 0*Biodegradation[1,PCE]*Conversion_Factor[PCE]
Contaminant_Production[1,TCE] = Biodegradation[1,PCE]*Conversion_Factor[PCE]
Contaminant_Production[1,DCE] = Biodegradation[1,TCE]*Conversion_Factor[TCE]
Contaminant_Production[1,VC] = Biodegradation[1,DCE]*Conversion_Factor[DCE]
Contaminant_Production[1,Ethene] = Biodegradation[1,VC]*Conversion_Factor[VC]
Contaminant_Production[2,PCE] = 0*Biodegradation[2,PCE]*Conversion_Factor[PCE]
Contaminant_Production[2,TCE] = Biodegradation[2,PCE]*Conversion_Factor[PCE]
Contaminant_Production[2,DCE] = Biodegradation[2,TCE]*Conversion_Factor[TCE]
Contaminant_Production[2,VC] = Biodegradation[2,DCE]*Conversion_Factor[DCE]
Contaminant_Production[2,Ethene] = Biodegradation[2,VC]*Conversion_Factor[VC]
Contaminant_Production[3,PCE] = 0*Biodegradation[2,PCE]*Conversion_Factor[PCE]
Contaminant_Production[3,TCE] = Biodegradation[3,PCE]*Conversion_Factor[PCE]
Contaminant_Production[3,DCE] = Biodegradation[3,TCE]*Conversion_Factor[TCE]
Contaminant_Production[3,VC] = Biodegradation[3,DCE]*Conversion_Factor[DCE]
Contaminant_Production[3,Ethene] = Biodegradation[3,VC]*Conversion_Factor[VC]
Contaminant_Production[4,PCE] = 0*Biodegradation[2,PCE]*Conversion_Factor[PCE]
Contaminant_Production[4,TCE] = Biodegradation[4,PCE]*Conversion_Factor[PCE]
Contaminant_Production[4,DCE] = Biodegradation[4,TCE]*Conversion_Factor[TCE]
Contaminant_Production[4,VC] = Biodegradation[4,DCE]*Conversion_Factor[DCE]
Contaminant_Production[4,Ethene] = Biodegradation[4,VC]*Conversion_Factor[VC]
Contaminant_Production[5,PCE] = 0*Biodegradation[2,PCE]*Conversion_Factor[PCE]
Contaminant_Production[5,TCE] = Biodegradation[5,PCE]*Conversion_Factor[PCE]
Contaminant_Production[5,DCE] = Biodegradation[5,TCE]*Conversion_Factor[TCE]
Contaminant_Production[5,VC] = Biodegradation[5,DCE]*Conversion_Factor[DCE]
Contaminant_Production[5,Ethene] = Biodegradation[5,VC]*Conversion_Factor[VC]
Contaminant_Production[6,PCE] = 0*Biodegradation[2,PCE]*Conversion_Factor[PCE]
Contaminant_Production[6,TCE] = Biodegradation[6,PCE]*Conversion_Factor[PCE]
Contaminant_Production[6,DCE] = Biodegradation[6,TCE]*Conversion_Factor[TCE]
Contaminant_Production[6,VC] = Biodegradation[6,DCE]*Conversion_Factor[DCE
Contaminant_Production[6,Ethene] = Biodegradation[6,VC]*Conversion_Factor[VC]
```

Contaminant_Production[7,PCE] = 0*Biodegradation[2,PCE]*Conversion_Factor[PCE]
Contaminant_Production[7,TCE] = Biodegradation[7,PCE]*Conversion_Factor[PCE]
Contaminant_Production[7,DCE] = Biodegradation[7,TCE]*Conversion_Factor[TCE]
Contaminant_Production[7,VC] = Biodegradation[7,DCE]*Conversion_Factor[DCE]
Contaminant_Production[7,Ethene] = Biodegradation[7,VC]*Conversion_Factor[VC]
Contaminant_Production[8,PCE] = 0*Biodegradation[2,PCE]*Conversion_Factor[PCE]
Contaminant_Production[8,TCE] = Biodegradation[8,PCE]*Conversion_Factor[PCE]
Contaminant_Production[8,DCE] = Biodegradation[8,TCE]*Conversion_Factor[TCE]
Contaminant_Production[8,VC] = Biodegradation[8,DCE]*Conversion_Factor[DCE]
Contaminant_Production[8,Ethene] = Biodegradation[8,VC]*Conversion_Factor[VC]
Contaminant_Production[9,PCE] = 0*Biodegradation[2,PCE]*Conversion_Factor[PCE]
Contaminant_Production[9,TCE] = Biodegradation[9,PCE]*Conversion_Factor[PCE]
Contaminant_Production[9,DCE] = Biodegradation[9,TCE]*Conversion_Factor[TCE]
Contaminant_Production[9,VC] = Biodegradation[9,DCE]*Conversion_Factor[DCE]
Contaminant_Production[9,Ethene] = Biodegradation[9,VC]*Conversion_Factor[VC]
Contaminant_Production[10,PCE] = 0*Biodegradation[2,PCE]*Conversion_Factor[PCE]
Contaminant_Production[10,TCE] = Biodegradation[10,PCE]*Conversion_Factor[PCE]
Contaminant_Production[10,DCE] = Biodegradation[10,TCE]*Conversion_Factor[TCE]
Contaminant_Production[10,VC] = Biodegradation[10,DCE]*Conversion_Factor[DCE]
Contaminant_Production[10,Ethene] = Biodegradation[10,VC]*Conversion_Factor[VC]
Contaminant_Production[11,PCE] = 0*Biodegradation[2,PCE]*Conversion_Factor[PCE]
Contaminant_Production[11,TCE] = Biodegradation[11,PCE]*Conversion_Factor[PCE]
Contaminant_Production[11,DCE] = Biodegradation[11,TCE]*Conversion_Factor[TCE]
Contaminant_Production[11,VC] = Biodegradation[11,DCE]*Conversion_Factor[DCE]
Contaminant_Production[11,Ethene] = Biodegradation[11,VC]*Conversion_Factor[VC]
Contaminant_Production[12,PCE] = 0*Biodegradation[2,PCE]*Conversion_Factor[PCE]
Contaminant_Production[12,TCE] = Biodegradation[12,PCE]*Conversion_Factor[PCE]
Contaminant_Production[12,DCE] = Biodegradation[12,TCE]*Conversion_Factor[TCE]
Contaminant_Production[12,VC] = Biodegradation[12,DCE]*Conversion_Factor[DCE]
Contaminant_Production[12,Ethene] = Biodegradation[12,VC]*Conversion_Factor[VC]
Contaminant_Production[13,PCE] = 0*Biodegradation[2,PCE]*Conversion_Factor[PCE]
Contaminant_Production[13,TCE] = Biodegradation[13,PCE]*Conversion_Factor[PCE]
Contaminant_Production[13,DCE] = Biodegradation[13,TCE]*Conversion_Factor[TCE]
Contaminant_Production[13,VC] = Biodegradation[13,DCE]*Conversion_Factor[DCE]
Contaminant_Production[13,Ethene] = Biodegradation[13,VC]*Conversion_Factor[VC]
Contaminant_Production[14,PCE] = 0*Biodegradation[2,PCE]*Conversion_Factor[PCE]
Contaminant_Production[14,TCE] = Biodegradation[14,PCE]*Conversion_Factor[PCE]
Contaminant_Production[14,DCE] = Biodegradation[14,TCE]*Conversion_Factor[TCE]
Contaminant_Production[14,VC] = Biodegradation[14,DCE]*Conversion_Factor[DCE]
Contaminant_Production[14,Ethene] = Biodegradation[14,VC]*Conversion_Factor[VC]
Contaminant_Production[15,PCE] = 0*Biodegradation[2,PCE]*Conversion_Factor[PCE]
Contaminant_Production[15,TCE] = Biodegradation[15,PCE]*Conversion_Factor[PCE]
Contaminant_Production[15,DCE] = Biodegradation[15,TCE]*Conversion_Factor[TCE]
Contaminant_Production[15,VC] = Biodegradation[15,DCE]*Conversion_Factor[DCE]
Contaminant_Production[15,Ethene] = Biodegradation[15,VC]*Conversion_Factor[VC]

Contaminant_Production[16,PCE] = 0*Biodegradation[2,PCE]*Conversion_Factor[PCE]
Contaminant_Production[16,TCE] = Biodegradation[16,PCE]*Conversion_Factor[PCE]
Contaminant_Production[16,DCE] = Biodegradation[16,TCE]*Conversion_Factor[TCE]
Contaminant_Production[16,VC] = Biodegradation[16,DCE]*Conversion_Factor[DCE]
Contaminant_Production[16,Ethene] = Biodegradation[16,VC]*Conversion_Factor[VC]
Contaminant_Production[17,PCE] = 0*Biodegradation[2,PCE]*Conversion_Factor[PCE]
Contaminant_Production[17,TCE] = Biodegradation[17,PCE]*Conversion_Factor[PCE]
Contaminant_Production[17,DCE] = Biodegradation[17,TCE]*Conversion_Factor[TCE]
Contaminant_Production[17,VC] = Biodegradation[17,DCE]*Conversion_Factor[DCE]
Contaminant_Production[17,Ethene] = Biodegradation[17,VC]*Conversion_Factor[VC]
Contaminant_Production[18,PCE] = 0*Biodegradation[2,PCE]*Conversion_Factor[PCE]
Contaminant_Production[18,TCE] = Biodegradation[18,PCE]*Conversion_Factor[PCE]
Contaminant_Production[18,DCE] = Biodegradation[18,TCE]*Conversion_Factor[TCE]
Contaminant_Production[18,VC] = Biodegradation[18,DCE]*Conversion_Factor[DCE]
Contaminant_Production[18,Ethene] = Biodegradation[18,VC]*Conversion_Factor[VC]

Outflows:

Contaminant_Out[Layer_Number,Contaminant] =
    Contaminant_Con[Layer_Number,Contaminant]*Flow
Biodegradation[Layer_Number,Contaminant] =
    (k[Contaminant]*Contaminant_Con[Layer_Number,Contaminant]*Layer_Biomass[Contaminant])/(Ks[Contaminant]+Contaminant_Con[Layer_Number,Contaminant])

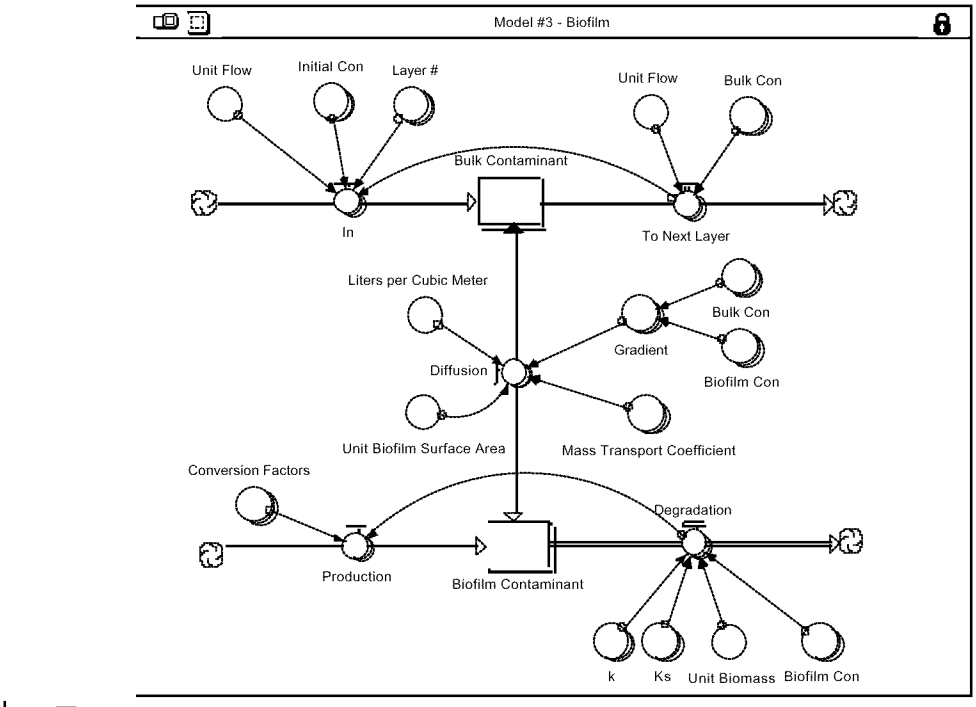
Parameters:

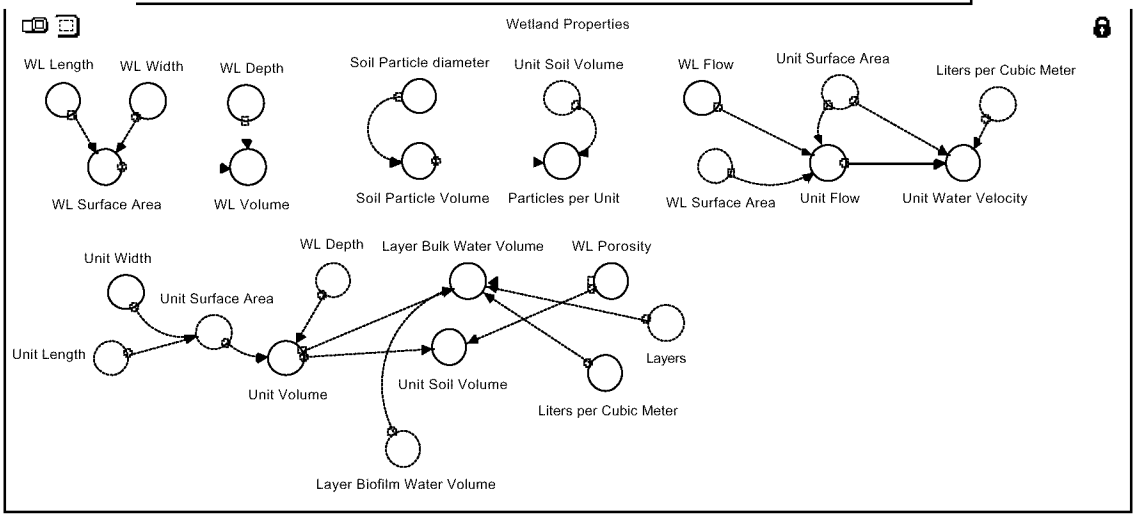
Contaminant_Con[Layer_Number,Contaminant] =
    TanksInSeries[Layer_Number,Contaminant]/Layer_Water_Vol
Conversion_Factor[PCE] = .79222
Conversion_Factor[TCE] = .737724
Conversion_Factor[DCE] = .644479
Conversion_Factor[VC] = .448359
Conversion_Factor[Ethene] = 0
Flow = .001026
Initial_Concentration[PCE] = .0005
Initial_Concentration[TCE] = 0
Initial_Concentration[DCE] = 0
Initial_Concentration[VC] = 0
Initial_Concentration[Ethene] = 0
k[PCE] = 8.292E-5
k[TCE] = 1.095E-4
k[DCE] = 8.075E-5
k[VC] = 5.21E-5
k[Ethene] = 0
Ks[PCE] = .0896
Ks[TCE] = .07096

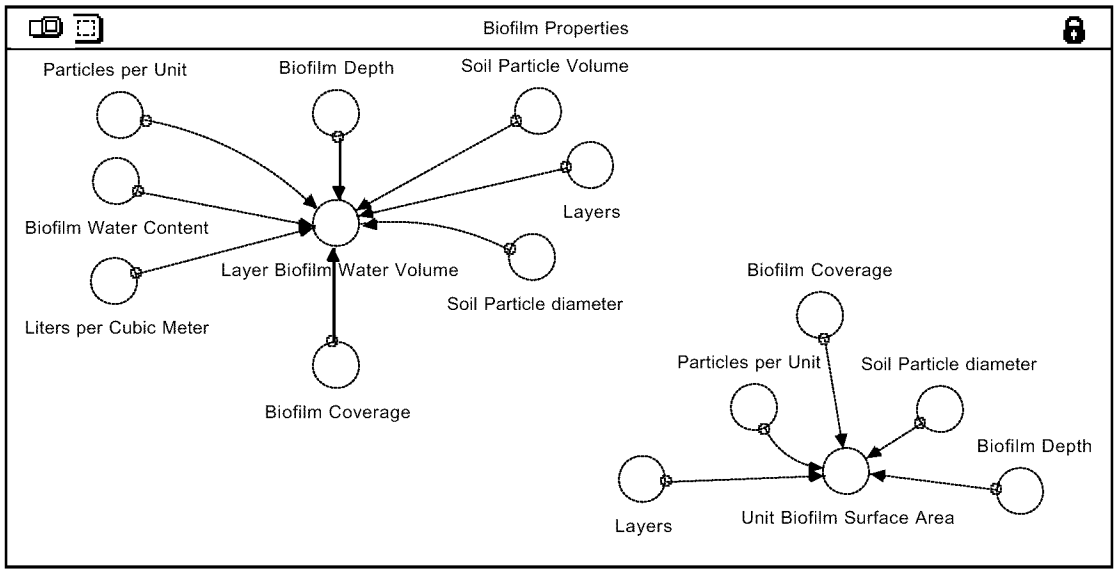
Ks[DCE] = .05233
Ks[VC] = 18.125
Ks[Ethene] = 1
Layers = 18
Layer_#[1] = 1
Layer_#[2] = 2
Layer_#[3] = 3
Layer_#[4] = 4
Layer_#[5] = 5
Layer_#[6] = 6
Layer_#[7] = 7
Layer_#[8] = 8
Layer_#[9] = 9
Layer_#[10] = 10
Layer_#[11] = 11
Layer_#[12] = 12
Layer_#[13] = 13
Layer_#[14] = 14
Layer_#[15] = 15
Layer_#[16] = 16
Layer_#[17] = 17
Layer_#[18] = 18
Layer_Biomass[Contaminant] = 2.258797

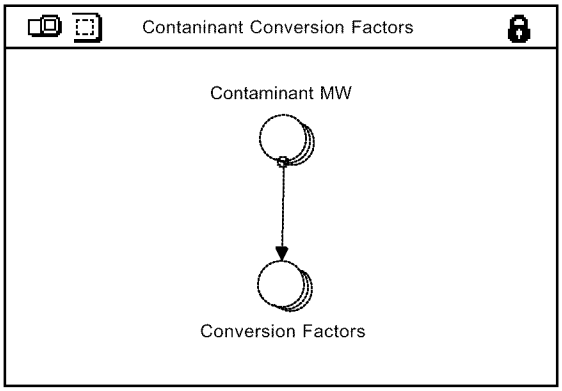
Wetland Parameters:
Layer_Water_Vol = (Unit_Volume*Soil_Porosity*Liters_in_Cubic_Meter)/Layers
Liters_in_Cubic_Meter = 1000
Soil_Porosity = .5
Unit_Length = 1
Unit_Volume = WL_Depth*Unit_Length*Unit_Width
Unit_Width = 1WL_Depth = .4572

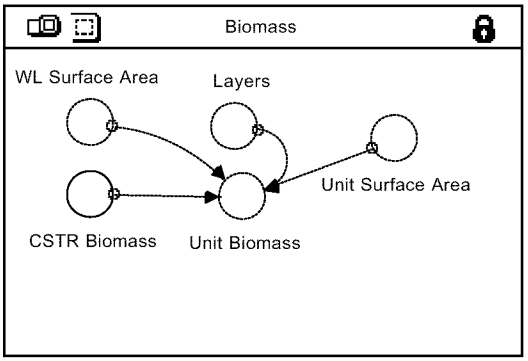
Appendix E – Model #3 STELLA Structure

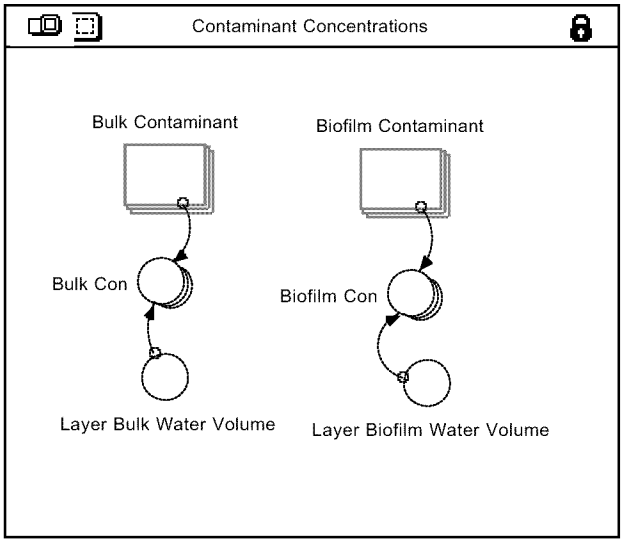





Biofilm Properties
Particles per Unit
Biofilm Depth
Soil Particle Volume
Layers
Biofilm Water Content
Layer Biofilm Water Volume
Soil Particle diameter
Liters per Cubic Meter
Biofilm Coverage
Biofilm Coverage
Particles per Unit
Soil Particle diameter
Biofilm Depth
Layers
Unit Biofilm Surface Area


Contaninant Conversion Factors
Contaminant MW
Conversion Factors


Biomass
WL Surface Area
Layers
Unit Surface Area
CSTR Biomass
Unit Biomass


Contaminant Concentrations
Bulk Contaminant
Biofilm Contaminant
Bulk Con
Biofilm Con
Layer Bulk Water Volume
Layer Biofilm Water Volume

Appendix F - Model #3 Equations

Biofilm Properties:

Biofilm_Coverage = .5
Biofilm_Depth = 1E-6
Biofilm_Water_Content = .9
Layer_Biofilm_Water_Volume =
    ((((4/3)*PI*((Soil_Particle_diameter/2)+Biofilm_Depth)^3)-
    Soil_Particle_Volume)*Biofilm_Coverage*Biofilm_Water_Content*Particles_per_Unit*Liters_per_Cubic_Meter)/Layers
Unit_Biofilm_Surface_Area =
    (((4*PI*((Soil_Particle_diameter/2)+Biofilm_Depth)^2)*Particles_per_Unit)/Layers)*Biofilm_Coverage

Biomass:

CSTR_Biomass = 25000
Unit_Biomass = (CSTR_Biomass*Unit_Surface_Area)/(WL_Surface_Area*Layers)

Contaminant Concentrations:

Biofilm_Con[Layer,Contaminant] =
    Biofilm_Contaminant[Layer,Contaminant]/Layer_Biofilm_Water_Volume
Bulk_Con[Layer,Contaminant] =
    Bulk_Contaminant[Layer,Contaminant]/Layer_Bulk_Water_Volume

Contaminant Conversion Factors:

Contaminant_MW[PCE] = 165.8
Contaminant_MW[TCE] = 131.35
Contaminant_MW[DCE] = 96.9
Contaminant_MW[VC] = 62.45
Contaminant_MW[Ethene] = 28
Conversion_Factors[PCE] = Contaminant_MW[TCE]/Contaminant_MW[PCE]
Conversion_Factors[TCE] = Contaminant_MW[DCE]/Contaminant_MW[TCE]
Conversion_Factors[DCE] = Contaminant_MW[VC]/Contaminant_MW[DCE]
Conversion_Factors[VC] = Contaminant_MW[Ethene]/Contaminant_MW[VC]
Conversion_Factors[Ethene] = 0/Contaminant_MW[Ethene]

Model #3 – Biofilm:

Biofilm Mass Balance:

Biofilm_Contaminant[Layer,Contaminant](t) =
    Biofilm_Contaminant[Layer,Contaminant](t - dt) +
    (Production[Layer,Contaminant] + Diffusion[Layer,Contaminant] -
    Degradation[Layer,Contaminant]) * dt
INIT Biofilm_Contaminant[Layer,Contaminant] = 0

Biofilm Inflows:

Production[1,PCE] = 0*Degradation[1,PCE]*Conversion_Factors[PCE]
Production[1,TCE] = Degradation[1,PCE]*Conversion_Factors[PCE]
Production[1,DCE] = Degradation[1,TCE]*Conversion_Factors[TCE]
Production[1,VC] = Degradation[1,DCE]*Conversion_Factors[DCE]
Production[1,Ethene] = Degradation[1,VC]*Conversion_Factors[VC]
Production[2,PCE] = 0*Degradation[1,PCE]*Conversion_Factors[PCE]
Production[2,TCE] = Degradation[2,PCE]*Conversion_Factors[PCE]
Production[2,DCE] = Degradation[2,TCE]*Conversion_Factors[TCE]
Production[2,VC] = Degradation[2,DCE]*Conversion_Factors[DCE]
Production[2,Ethene] = Degradation[2,VC]*Conversion_Factors[VC]
Production[3,PCE] = 0*Degradation[1,PCE]*Conversion_Factors[PCE]
Production[3,TCE] = Degradation[3,PCE]*Conversion_Factors[PCE]
Production[3,DCE] = Degradation[3,TCE]*Conversion_Factors[TCE]
Production[3,VC] = Degradation[3,DCE]*Conversion_Factors[DCE]
Production[3,Ethene] = Degradation[3,VC]*Conversion_Factors[VC]
Production[4,PCE] = 0*Degradation[1,PCE]*Conversion_Factors[PCE]
Production[4,TCE] = Degradation[4,PCE]*Conversion_Factors[PCE]
Production[4,DCE] = Degradation[4,TCE]*Conversion_Factors[TCE]
Production[4,VC] = Degradation[4,DCE]*Conversion_Factors[DCE]
Production[4,Ethene] = Degradation[4,VC]*Conversion_Factors[VC]
Production[5,PCE] = 0*Degradation[1,PCE]*Conversion_Factors[PCE]
Production[5,TCE] = Degradation[5,PCE]*Conversion_Factors[PCE]
Production[5,DCE] = Degradation[5,TCE]*Conversion_Factors[TCE]
Production[5,VC] = Degradation[5,DCE]*Conversion_Factors[DCE]
Production[5,Ethene] = Degradation[5,VC]*Conversion_Factors[VC]
Production[6,PCE] = 0*Degradation[1,PCE]*Conversion_Factors[PCE]
Production[6,TCE] = Degradation[6,PCE]*Conversion_Factors[PCE]
Production[6,DCE] = Degradation[6,TCE]*Conversion_Factors[TCE]
Production[6,VC] = Degradation[6,DCE]*Conversion_Factors[DCE]
Production[6,Ethene] = Degradation[6,VC]*Conversion_Factors[VC]
Production[7,PCE] = 0*Degradation[1,PCE]*Conversion_Factors[PCE]
Production[7,TCE] = Degradation[7,PCE]*Conversion_Factors[PCE]
Production[7,DCE] = Degradation[7,TCE]*Conversion_Factors[TCE]
Production[7,VC] = Degradation[7,DCE]*Conversion_Factors[DCE]
Production[7,Ethene] = Degradation[7,VC]*Conversion_Factors[VC]
Production[8,PCE] = 0*Degradation[1,PCE]*Conversion_Factors[PCE]
Production[8,TCE] = Degradation[8,PCE]*Conversion_Factors[PCE]
Production[8,DCE] = Degradation[8,TCE]*Conversion_Factors[TCE]
Production[8,VC] = Degradation[8,DCE]*Conversion_Factors[DCE]
Production[8,Ethene] = Degradation[8,VC]*Conversion_Factors[VC]
Production[9,PCE] = 0*Degradation[1,PCE]*Conversion_Factors[PCE]
Production[9,TCE] = Degradation[9,PCE]*Conversion_Factors[PCE]
Production[9,DCE] = Degradation[9,TCE]*Conversion_Factors[TCE]
Production[9,VC] = Degradation[9,DCE]*Conversion_Factors[DCE]

Production[9,Ethene] = Degradation[9,VC]*Conversion_Factors[VC]
Production[10,PCE] = 0*Degradation[1,PCE]*Conversion_Factors[PCE]
Production[10,TCE] = Degradation[10,PCE]*Conversion_Factors[PCE]
Production[10,DCE] = Degradation[10,TCE]*Conversion_Factors[TCE]
Production[10,VC] = Degradation[10,DCE]*Conversion_Factors[DCE]
Production[10,Ethene] = Degradation[10,VC]*Conversion_Factors[VC]
Production[11,PCE] = 0*Degradation[1,PCE]*Conversion_Factors[PCE]
Production[11,TCE] = Degradation[11,PCE]*Conversion_Factors[PCE]
Production[11,DCE] = Degradation[11,TCE]*Conversion_Factors[TCE]
Production[11,VC] = Degradation[11,DCE]*Conversion_Factors[DCE]
Production[11,Ethene] = Degradation[11,VC]*Conversion_Factors[VC]
Production[12,PCE] = 0*Degradation[1,PCE]*Conversion_Factors[PCE]
Production[12,TCE] = Degradation[12,PCE]*Conversion_Factors[PCE]
Production[12,DCE] = Degradation[12,TCE]*Conversion_Factors[TCE]
Production[12,VC] = Degradation[12,DCE]*Conversion_Factors[DCE]
Production[12,Ethene] = Degradation[12,VC]*Conversion_Factors[VC]
Production[13,PCE] = 0*Degradation[1,PCE]*Conversion_Factors[PCE]
Production[13,TCE] = Degradation[13,PCE]*Conversion_Factors[PCE]
Production[13,DCE] = Degradation[13,TCE]*Conversion_Factors[TCE]
Production[13,VC] = Degradation[13,DCE]*Conversion_Factors[DCE]
Production[13,Ethene] = Degradation[13,VC]*Conversion_Factors[VC]
Production[14,PCE] = 0*Degradation[1,PCE]*Conversion_Factors[PCE]
Production[14,TCE] = Degradation[14,PCE]*Conversion_Factors[PCE]
Production[14,DCE] = Degradation[14,TCE]*Conversion_Factors[TCE]
Production[14,VC] = Degradation[14,DCE]*Conversion_Factors[DCE]
Production[14,Ethene] = Degradation[14,VC]*Conversion_Factors[VC]
Production[15,PCE] = 0*Degradation[1,PCE]*Conversion_Factors[PCE]
Production[15,TCE] = Degradation[15,PCE]*Conversion_Factors[PCE]
Production[15,DCE] = Degradation[15,TCE]*Conversion_Factors[TCE]
Production[15,VC] = Degradation[15,DCE]*Conversion_Factors[DCE]
Production[15,Ethene] = Degradation[15,VC]*Conversion_Factors[VC]
Production[16,PCE] = 0*Degradation[1,PCE]*Conversion_Factors[PCE]
Production[16,TCE] = Degradation[16,PCE]*Conversion_Factors[PCE]
Production[16,DCE] = Degradation[16,TCE]*Conversion_Factors[TCE]
Production[16,VC] = Degradation[16,DCE]*Conversion_Factors[DCE]
Production[16,Ethene] = Degradation[16,VC]*Conversion_Factors[VC]
Production[17,PCE] = 0*Degradation[1,PCE]*Conversion_Factors[PCE]
Production[17,TCE] = Degradation[17,PCE]*Conversion_Factors[PCE]
Production[17,DCE] = Degradation[17,TCE]*Conversion_Factors[TCE]
Production[17,VC] = Degradation[17,DCE]*Conversion_Factors[DCE]
Production[17,Ethene] = Degradation[17,VC]*Conversion_Factors[VC]
Production[18,PCE] = 0*Degradation[1,PCE]*Conversion_Factors[PCE]
Production[18,TCE] = Degradation[18,PCE]*Conversion_Factors[PCE]
Production[18,DCE] = Degradation[18,TCE]*Conversion_Factors[TCE]
Production[18,VC] = Degradation[18,DCE]*Conversion_Factors[DCE]

```
Production[18,Ethene] = Degradation[18,VC]*Conversion_Factors[VC]
Diffusion[Layer,Contaminant] =
        Gradient[Layer,Contaminant]*Mass_Transport_Coefficient[Contaminant]*Liters
        _per_Cubic_Meter*Unit_Biofilm_Surface_Area
```

Biofilm Outflows:

```
Degradation[Layer,Contaminant] =
        (k[Contaminant]*Biofilm_Con[Layer,Contaminant]*Unit_Biomass)/(Ks[Contami
        nant]+Biofilm_Con[Layer,Contaminant])
```

Bulk Mass Balance:

```
Bulk_Contaminant[Layer,Contaminant](t) = Bulk_Contaminant[Layer,Contaminant](t –
        dt) + (In[Layer,Contaminant] - To_Next_Layer[Layer,Contaminant] -
        Diffusion[Layer,Contaminant]) * dt
INIT Bulk_Contaminant[Layer,Contaminant] = 0
```

Bulk Inflows:

```
In[1,PCE] = IF(Layer_#[1]=1)
        THEN(Initial_Con[PCE]*Unit_Flow)
        ELSE(To_Next_Layer[1,PCE])
In[1,TCE] = IF(Layer_#[1]=1)
        THEN(Initial_Con[TCE]*Unit_Flow)
        ELSE(To_Next_Layer[1,TCE])
In[1,DCE] = IF(Layer_#[1]=1)
        THEN(Initial_Con[DCE]*Unit_Flow)
        ELSE(To_Next_Layer[1,DCE])
In[1,VC] = IF(Layer_#[1]=1)
        THEN(Initial_Con[VC]*Unit_Flow)
        ELSE(To_Next_Layer[1,VC])
In[1,Ethene] = IF(Layer_#[1]=1)
        THEN(Initial_Con[Ethene]*Unit_Flow)
        ELSE(To_Next_Layer[1,Ethene])
In[2,PCE] = IF(Layer_#[2]=1)
        THEN(Initial_Con[PCE]*Unit_Flow)
        ELSE(To_Next_Layer[1,PCE])
In[2,TCE] = IF(Layer_#[2]=1)
        THEN(Initial_Con[TCE]*Unit_Flow)
        ELSE(To_Next_Layer[1,TCE])
In[2,DCE] = IF(Layer_#[2]=1)
        THEN(Initial_Con[DCE]*Unit_Flow)
        ELSE(To_Next_Layer[1,DCE])
In[2,VC] = IF(Layer_#[2]=1)
        THEN(Initial_Con[VC]*Unit_Flow)
        ELSE(To_Next_Layer[1,VC])
```

```
In[2,Ethene] = IF(Layer_#[2]=1)
        THEN(Initial_Con[Ethene]*Unit_Flow)
        ELSE(To_Next_Layer[1,Ethene])
In[3,PCE] = IF(Layer_#[3]=1)
        THEN(Initial_Con[PCE]*Unit_Flow)
        ELSE(To_Next_Layer[2,PCE])
In[3,TCE] = IF(Layer_#[3]=1)
        THEN(Initial_Con[TCE]*Unit_Flow)
        ELSE(To_Next_Layer[2,TCE])
In[3,DCE] = IF(Layer_#[3]=1)
        THEN(Initial_Con[DCE]*Unit_Flow)
        ELSE(To_Next_Layer[2,DCE])
In[3,VC] = IF(Layer_#[3]=1)
        THEN(Initial_Con[VC]*Unit_Flow)
        ELSE(To_Next_Layer[2,VC])
In[3,Ethene] = IF(Layer_#[3]=1)
        THEN(Initial_Con[Ethene]*Unit_Flow)
        ELSE(To_Next_Layer[2,Ethene])
In[4,PCE] = IF(Layer_#[4]=1)
        THEN(Initial_Con[PCE]*Unit_Flow)
        ELSE(To_Next_Layer[3,PCE])
In[4,TCE] = IF(Layer_#[4]=1)
        THEN(Initial_Con[TCE]*Unit_Flow)
        ELSE(To_Next_Layer[3,TCE])
In[4,DCE] = IF(Layer_#[4]=1)
        THEN(Initial_Con[DCE]*Unit_Flow)
        ELSE(To_Next_Layer[3,DCE])
In[4,VC] = IF(Layer_#[4]=1)
        THEN(Initial_Con[VC]*Unit_Flow)
        ELSE(To_Next_Layer[3,VC])
In[4,Ethene] = IF(Layer_#[4]=1)
        THEN(Initial_Con[Ethene]*Unit_Flow)
        ELSE(To_Next_Layer[3,Ethene])
In[5,PCE] = IF(Layer_#[5]=1)
        THEN(Initial_Con[PCE]*Unit_Flow)
        ELSE(To_Next_Layer[4,PCE])
In[5,TCE] = IF(Layer_#[5]=1)
        THEN(Initial_Con[TCE]*Unit_Flow)
        ELSE(To_Next_Layer[4,TCE])
In[5,DCE] = IF(Layer_#[5]=1)
        THEN(Initial_Con[DCE]*Unit_Flow)
        ELSE(To_Next_Layer[4,DCE])
In[5,VC] = IF(Layer_#[5]=1)
        THEN(Initial_Con[VC]*Unit_Flow)
        ELSE(To_Next_Layer[4,VC])
```

```
In[5,Ethene] = IF(Layer_#[5]=1)
        THEN(Initial_Con[Ethene]*Unit_Flow)
        ELSE(To_Next_Layer[4,Ethene])
In[6,PCE] = IF(Layer_#[6]=1)
        THEN(Initial_Con[PCE]*Unit_Flow)
        ELSE(To_Next_Layer[5,PCE])
In[6,TCE] = IF(Layer_#[6]=1)
        THEN(Initial_Con[TCE]*Unit_Flow)
        ELSE(To_Next_Layer[5,TCE])
In[6,DCE] = IF(Layer_#[6]=1)
        THEN(Initial_Con[DCE]*Unit_Flow)
        ELSE(To_Next_Layer[5,DCE])
In[6,VC] = IF(Layer_#[6]=1)
        THEN(Initial_Con[VC]*Unit_Flow)
        ELSE(To_Next_Layer[5,VC])
In[6,Ethene] = IF(Layer_#[6]=1)
        THEN(Initial_Con[Ethene]*Unit_Flow)
        ELSE(To_Next_Layer[5,Ethene])
In[7,PCE] = IF(Layer_#[7]=1)
        THEN(Initial_Con[PCE]*Unit_Flow)
        ELSE(To_Next_Layer[6,PCE])
In[7,TCE] = IF(Layer_#[7]=1)
        THEN(Initial_Con[TCE]*Unit_Flow)
        ELSE(To_Next_Layer[6,TCE])
In[7,DCE] = IF(Layer_#[7]=1)
        THEN(Initial_Con[DCE]*Unit_Flow)
        ELSE(To_Next_Layer[6,DCE])
In[7,VC] = IF(Layer_#[7]=1)
        THEN(Initial_Con[VC]*Unit_Flow)
        ELSE(To_Next_Layer[6,VC])
In[7,Ethene] = IF(Layer_#[7]=1)
        THEN(Initial_Con[Ethene]*Unit_Flow)
        ELSE(To_Next_Layer[6,Ethene])
In[8,PCE] = IF(Layer_#[8]=1)
        THEN(Initial_Con[PCE]*Unit_Flow)
        ELSE(To_Next_Layer[7,PCE])
In[8,TCE] = IF(Layer_#[8]=1)
        THEN(Initial_Con[TCE]*Unit_Flow)
        ELSE(To_Next_Layer[7,TCE])
In[8,DCE] = IF(Layer_#[8]=1)
        THEN(Initial_Con[DCE]*Unit_Flow)
        ELSE(To_Next_Layer[7,DCE])
In[8,VC] = IF(Layer_#[8]=1)
        THEN(Initial_Con[VC]*Unit_Flow)
        ELSE(To_Next_Layer[7,VC])
```

```
In[8,Ethene] = IF(Layer_#[8]=1)
        THEN(Initial_Con[Ethene]*Unit_Flow)
        ELSE(To_Next_Layer[7,Ethene])
In[9,PCE] = IF(Layer_#[9]=1)
        THEN(Initial_Con[PCE]*Unit_Flow)
        ELSE(To_Next_Layer[8,PCE])
In[9,TCE] = IF(Layer_#[9]=1)
        THEN(Initial_Con[TCE]*Unit_Flow)
        ELSE(To_Next_Layer[8,TCE])
In[9,DCE] = IF(Layer_#[9]=1)
        THEN(Initial_Con[DCE]*Unit_Flow)
        ELSE(To_Next_Layer[8,DCE])
In[9,VC] = IF(Layer_#[9]=1)
        THEN(Initial_Con[VC]*Unit_Flow)
        ELSE(To_Next_Layer[8,VC])
In[9,Ethene] = IF(Layer_#[9]=1)
        THEN(Initial_Con[Ethene]*Unit_Flow)
        ELSE(To_Next_Layer[8,Ethene])
In[10,PCE] = IF(Layer_#[10]=1)
        THEN(Initial_Con[PCE]*Unit_Flow)
        ELSE(To_Next_Layer[9,PCE])
In[10,TCE] = IF(Layer_#[10]=1)
        THEN(Initial_Con[TCE]*Unit_Flow)
        ELSE(To_Next_Layer[9,TCE])
In[10,DCE] = IF(Layer_#[10]=1)
        THEN(Initial_Con[DCE]*Unit_Flow)
        ELSE(To_Next_Layer[9,DCE])
In[10,VC] = IF(Layer_#[10]=1)
        THEN(Initial_Con[VC]*Unit_Flow)
        ELSE(To_Next_Layer[9,VC])
In[10,Ethene] = IF(Layer_#[10]=1)
        THEN(Initial_Con[Ethene]*Unit_Flow)
        ELSE(To_Next_Layer[9,Ethene])
In[11,PCE] = IF(Layer_#[11]=1)
        THEN(Initial_Con[PCE]*Unit_Flow)
        ELSE(To_Next_Layer[10,PCE])
In[11,TCE] = IF(Layer_#[11]=1)
        THEN(Initial_Con[TCE]*Unit_Flow)
        ELSE(To_Next_Layer[10,TCE])
In[11,DCE] = IF(Layer_#[11]=1)
        THEN(Initial_Con[DCE]*Unit_Flow)
        ELSE(To_Next_Layer[10,DCE])
In[11,VC] = IF(Layer_#[11]=1)
        THEN(Initial_Con[VC]*Unit_Flow)
        ELSE(To_Next_Layer[10,VC])
```

```
In[11,Ethene] = IF(Layer_#[11]=1)
        THEN(Initial_Con[Ethene]*Unit_Flow)
        ELSE(To_Next_Layer[10,Ethene])
In[12,PCE] = IF(Layer_#[12]=1)
        THEN(Initial_Con[PCE]*Unit_Flow)
        ELSE(To_Next_Layer[11,PCE])
In[12,TCE] = IF(Layer_#[12]=1)
        THEN(Initial_Con[TCE]*Unit_Flow)
        ELSE(To_Next_Layer[11,TCE])
In[12,DCE] = IF(Layer_#[12]=1)
        THEN(Initial_Con[DCE]*Unit_Flow)
        ELSE(To_Next_Layer[11,DCE])
In[12,VC] = IF(Layer_#[12]=1)
        THEN(Initial_Con[VC]*Unit_Flow)
        ELSE(To_Next_Layer[11,VC])
In[12,Ethene] = IF(Layer_#[12]=1)
        THEN(Initial_Con[Ethene]*Unit_Flow)
        ELSE(To_Next_Layer[11,Ethene])
In[13,PCE] = IF(Layer_#[13]=1)
        THEN(Initial_Con[PCE]*Unit_Flow)
        ELSE(To_Next_Layer[12,PCE])
In[13,TCE] = IF(Layer_#[13]=1)
        THEN(Initial_Con[TCE]*Unit_Flow)
        ELSE(To_Next_Layer[12,TCE])
In[13,DCE] = IF(Layer_#[13]=1)
        THEN(Initial_Con[DCE]*Unit_Flow)
        ELSE(To_Next_Layer[12,DCE])
In[13,VC] = IF(Layer_#[13]=1)
        THEN(Initial_Con[VC]*Unit_Flow)
        ELSE(To_Next_Layer[12,VC])
In[13,Ethene] = IF(Layer_#[13]=1)
        THEN(Initial_Con[Ethene]*Unit_Flow)
        ELSE(To_Next_Layer[12,Ethene])
In[14,PCE] = IF(Layer_#[14]=1)
        THEN(Initial_Con[PCE]*Unit_Flow)
        ELSE(To_Next_Layer[13,PCE])
In[14,TCE] = IF(Layer_#[14]=1)
        THEN(Initial_Con[TCE]*Unit_Flow)
        ELSE(To_Next_Layer[13,TCE])
In[14,DCE] = IF(Layer_#[14]=1)
        THEN(Initial_Con[DCE]*Unit_Flow)
        ELSE(To_Next_Layer[13,DCE])
In[14,VC] = IF(Layer_#[14]=1)
        THEN(Initial_Con[VC]*Unit_Flow)
        ELSE(To_Next_Layer[13,VC])
```

```
In[14,Ethene] = IF(Layer_#[14]=1)
        THEN(Initial_Con[Ethene]*Unit_Flow)
        ELSE(To_Next_Layer[13,Ethene])
In[15,PCE] = IF(Layer_#[15]=1)
        THEN(Initial_Con[PCE]*Unit_Flow)
        ELSE(To_Next_Layer[14,PCE])
In[15,TCE] = IF(Layer_#[15]=1)
        THEN(Initial_Con[TCE]*Unit_Flow)
        ELSE(To_Next_Layer[14,TCE])
In[15,DCE] = IF(Layer_#[15]=1)
        THEN(Initial_Con[DCE]*Unit_Flow)
        ELSE(To_Next_Layer[14,DCE])
In[15,VC] = IF(Layer_#[15]=1)
        THEN(Initial_Con[VC]*Unit_Flow)
        ELSE(To_Next_Layer[14,VC])
In[15,Ethene] = IF(Layer_#[15]=1)
        THEN(Initial_Con[Ethene]*Unit_Flow)
        ELSE(To_Next_Layer[14,Ethene])
In[16,PCE] = IF(Layer_#[16]=1)
        THEN(Initial_Con[PCE]*Unit_Flow)
        ELSE(To_Next_Layer[15,PCE])
In[16,TCE] = IF(Layer_#[16]=1)
        THEN(Initial_Con[TCE]*Unit_Flow)
        ELSE(To_Next_Layer[15,TCE])
In[16,DCE] = IF(Layer_#[16]=1)
        THEN(Initial_Con[DCE]*Unit_Flow)
        ELSE(To_Next_Layer[15,DCE])
In[16,VC] = IF(Layer_#[16]=1)
        THEN(Initial_Con[VC]*Unit_Flow)
        ELSE(To_Next_Layer[15,VC])
In[16,Ethene] = IF(Layer_#[16]=1)
        THEN(Initial_Con[Ethene]*Unit_Flow)
        ELSE(To_Next_Layer[15,Ethene])
In[17,PCE] = IF(Layer_#[17]=1)
        THEN(Initial_Con[PCE]*Unit_Flow)
        ELSE(To_Next_Layer[16,PCE])
In[17,TCE] = IF(Layer_#[17]=1)
        THEN(Initial_Con[TCE]*Unit_Flow)
        ELSE(To_Next_Layer[16,TCE])
In[17,DCE] = IF(Layer_#[17]=1)
        THEN(Initial_Con[DCE]*Unit_Flow)
        ELSE(To_Next_Layer[16,DCE])
In[17,VC] = IF(Layer_#[17]=1)
        THEN(Initial_Con[VC]*Unit_Flow)
        ELSE(To_Next_Layer[16,VC])
```

In[17,Ethene] = IF(Layer_#[17]=1)
THEN(Initial_Con[Ethene]*Unit_Flow)
ELSE(To_Next_Layer[16,Ethene])
In[18,PCE] = IF(Layer_#[18]=1)
THEN(Initial_Con[PCE]*Unit_Flow)
ELSE(To_Next_Layer[17,PCE])
In[18,TCE] = IF(Layer_#[18]=1)
THEN(Initial_Con[TCE]*Unit_Flow)
ELSE(To_Next_Layer[17,TCE])
In[18,DCE] = IF(Layer_#[18]=1)
THEN(Initial_Con[DCE]*Unit_Flow)
ELSE(To_Next_Layer[17,DCE])
In[18,VC] = IF(Layer_#[18]=1)
THEN(Initial_Con[VC]*Unit_Flow)
ELSE(To_Next_Layer[17,VC])
In[18,Ethene] = IF(Layer_#[18]=1)
THEN(Initial_Con[Ethene]*Unit_Flow)
ELSE(To_Next_Layer[17,Ethene])

Bulk Outflows:
To_Next_Layer[Layer,Contaminant] = Bulk_Con[Layer,Contaminant]*Unit_Flow
Diffusion[Layer,Contaminant] =
Gradient[Layer,Contaminant]*Mass_Transport_Coefficient[Contaminant]*Liters
_per_Cubic_Meter*Unit_Biofilm_Surface_Area
Gradient[Layer,Contaminant] = Bulk_Con[Layer,Contaminant]-
Biofilm_Con[Layer,Contaminant]

Parameter Values:
Initial_Con[PCE] = .0005
Initial_Con[TCE] = 0
Initial_Con[DCE] = 0
Initial_Con[VC] = 0
Initial_Con[Ethene] = 0
k[PCE] = 8.292E-5
k[TCE] = 1.095E-4
k[DCE] = 8.075E-5
k[VC] = 5.21E-5
k[Ethene] = 0
Ks[PCE] = .0896
Ks[TCE] = .07096
Ks[DCE] = .05233
Ks[VC] = 18.125
Ks[Ethene] = 1
Layer_#[1] = 1
Layer_#[2] = 2

Layer_#[3] = 3
Layer_#[4] = 4
Layer_#[5] = 5
Layer_#[6] = 6
Layer_#[7] = 7
Layer_#[8] = 8
Layer_#[9] = 9
Layer_#[10] = 10
Layer_#[11] = 11
Layer_#[12] = 12
Layer_#[13] = 13
Layer_#[14] = 14
Layer_#[15] = 15
Layer_#[16] = 16
Layer_#[17] = 17
Layer_#[18] = 18
Mass_Transport_Coefficient[PCE] = 3.154E-6
Mass_Transport_Coefficient[TCE] = 3.407E-6
Mass_Transport_Coefficient[DCE] = 3.9E-6
Mass_Transport_Coefficient[VC] = 4.1E-6
Mass_Transport_Coefficient[Ethene] = 5.714E-6

Wetland Properties:

Layers = 18
Layer_Bulk_Water_Volume =
((Unit_Volume*WL_Porosity*Liters_per_Cubic_Meter)/Layers)-
Layer_Biofilm_Water_Volume
Liters_per_Cubic_Meter = 1000
Particles_per_Unit = Unit_Soil_Volume/Soil_Particle_Volume
Soil_Particle_diameter = .001
Soil_Particle_Volume = (4/3)*PI*(Soil_Particle_diameter/2)^3
Unit_Flow = (WL_Flow*Unit_Surface_Area)/WL_Surface_Area
Unit_Length = 1
Unit_Soil_Volume = Unit_Volume*(1-WL_Porosity)
Unit_Surface_Area = Unit_Length*Unit_Width
Unit_Volume = Unit_Surface_Area*WL_Depth
Unit_Water_Velocity = (Unit_Flow/Liters_per_Cubic_Meter)/Unit_Surface_Area
Unit_Width = 1
WL_Depth = .4572
WL_Flow = .631
WL_Length = 36.6
WL_Porosity = .5
WL_Surface_Area = WL_Length*WL_Width
WL_Volume = WL_Surface_Area*WL_Depth
WL_Width = 16.8

Appendix G – Characteristic Time Scale Calculations

Calculating the characteristic reaction time scale.....

$$\tau_{rxn} := \frac{1}{k_{aPCE}}$$ [redacted]

Characteristic Mass Transfer Time Scale for PCE

$$k_c := 3.154 \cdot 10^{-6} \frac{m}{sec} \qquad L_b := 2.6 \cdot 10^{-4} m$$

$$\tau_{mt} := \frac{L_b}{k_c}$$ [redacted]

Calculation of the Damkohler number

$$D_A := \frac{\tau_{mt}}{\tau_{rxn}}$$ [redacted]

Since the Damkohler number is less than 10, the system with a mass tansfer coefficient of 3.154 x 10^{-6} is closely approximated by a tanks-in-series model.

Appendix H – *Second Damköhler Number* Calculations

Calculating the Damkohler number when $k_c = 3.154 \times 10^{-7}$

First we find the diffusion coefficient using new k_c value.....

$$v := 1.03 \cdot 10^{-6} \frac{m}{sec} \qquad Re := 4.104 \cdot 10^{-3} \qquad k_c := 3.154 \cdot 10^{-7} \frac{m}{sec}$$

$$\nu := 1.004 \cdot 10^{-6} \frac{m^2}{sec} \qquad Sc := \left(\frac{5.7 \cdot v}{Re^{\frac{3}{4}} \cdot k_c} \right)^{\frac{3}{2}} \qquad Sc = 3.89 \times 10^4$$

$$D_{ab} := \frac{\nu}{Sc}$$ [redacted]

Now we find the depth of the stagnant liquid layer with new diffusion coefficient value....

$$L_b := \frac{D_{ab} \cdot Re^{\frac{3}{4}} \cdot Sc^{\frac{2}{3}}}{5.7 \cdot v}$$ [redacted]

Next, we solve for the characteristic mass transfer time scale with new k_c and L_b....

$$\tau_{mt} := \frac{L_b}{k_c}$$ [redacted]

Finally, we solve for the Damkohler number.....

$$D_A := \frac{\tau_{mt}}{\tau_{rxn}}$$ [redacted]

This Damkohler number is greater then 10, so we would use Model #3 to model the system. This result agrees with the results shown in Figure 4.10. We can see that the spatial concentration profile for the system with $k_c = 3.154 \times 10^{-7}$ starts to depart from the spatial concentration profile of the reaction-limited case (Model #2), indicating that mass transfer limitations are starting to have an effect on effluent concentrations.

Calculating the Damkohler number when $k_c = 3.154 \times 10^{-8}$

First we find the diffusion coefficient using new k_c value.....

$$v := 1.03 \cdot 10^{-6} \frac{m}{sec} \qquad Re := 4.104 \cdot 10^{-3} \qquad k_c := 3.154 \cdot 10^{-8} \frac{m}{sec}$$

$$\nu := 1.004 \cdot 10^{-6} \frac{m^2}{sec} \qquad Sc := \left(\frac{5.7 \cdot v}{Re^{\frac{3}{4}} \cdot k_c} \right)^{\frac{3}{2}} \qquad Sc = 1.23 \times 10^{6}$$

$$D_{ab} := \frac{\nu}{Sc}$$

[redacted]

Now we find the depth of the stagnant liquid layer with new diffusion coefficient value....

$$L_b := \frac{D_{ab} \cdot Re^{\frac{3}{4}} \cdot Sc^{\frac{2}{3}}}{5.7 \cdot v}$$

[redacted]

Next, we solve for the characteristic mass transfer time scale with new k_c and L_b....

$$\tau_{mt} := \frac{L_b}{k_c}$$

[redacted]

Finally, we solve for the Damkohler number.....

$$D_A := \frac{\tau_{mt}}{\tau_{rxn}}$$

[redacted]

This Damkohler number is greater then 10, so we would use Model #3 to model the system. This result agrees with the results shown in Figure 4.10. We can see that the spatial concentration profile for the system with $k_c = 3.154 \times 10^{-8}$ starts to depart from the spatial concentration profile of the reaction-limited case (Model #2), indicating that mass transfer limitations are starting to have an effect on effluent concentrations.

Calculating the Damkohler number when $k_c = 3.154 \times 10^{-9}$

First we find the diffusion coefficient using new k_c value.....

$$v := 1.03 \cdot 10^{-6} \frac{m}{sec} \qquad Re := 4.104 \cdot 10^{-3} \qquad k_c := 3.154 \cdot 10^{-9} \frac{m}{sec}$$

$$\nu := 1.004 \cdot 10^{-6} \frac{m^2}{sec} \qquad Sc := \left(\frac{5.7 \cdot \nu}{Re^{\frac{3}{4}} \cdot k_c} \right)^{\frac{3}{2}} \qquad Sc = 3.89 \times 10^{7}$$

$$D_{ab} := \frac{\nu}{Sc}$$

[redacted]

Now we find the depth of the stagnant liquid layer with new diffusion coefficient value....

$$L_b := \frac{D_{ab} \cdot Re^{\frac{3}{4}} \cdot Sc^{\frac{2}{3}}}{5.7 \cdot v}$$

[redacted]

Next, we solve for the characteristic mass transfer time scale with new k_c and L_b....

$$\tau_{mt} := \frac{L_b}{k_c}$$

[redacted]

Finally, we solve for the Damkohler number.....

$$D_A := \frac{\tau_{mt}}{\tau_{rxn}}$$

[redacted]

This Damkohler number is greater then 10, so we would use Model #3 to model the system. This result agrees with the results shown in Figure 4.10. We can see that the spatial concentration profile for the system with $k_c = 3.154 \times 10^{-9}$ starts to depart from the spatial concentration profile of the reaction-limited case (Model #2), indicating that mass transfer limitations are starting to have an effect on effluent concentrations.

Calculating the Damkohler number when $k_c = 3.154 \times 10^{-5}$

First we find the diffusion coefficient using new k_c value.....

$$v := 1.03 \cdot 10^{-6} \frac{m}{sec} \qquad Re := 4.104 \cdot 10^{-3} \qquad k_c := 3.154 \cdot 10^{-5} \frac{m}{sec}$$

$$\nu := 1.004 \cdot 10^{-6} \frac{m^2}{sec} \qquad Sc := \left(\frac{5.7 \cdot v}{Re^{\frac{3}{4}} \cdot k_c} \right)^{\frac{3}{2}} \qquad Sc = 38.897$$

$$D_{ab} := \frac{\nu}{Sc}$$

[redacted]

Now we find the depth of the stagnant liquid layer with new diffusion coefficient value....

$$L_b := \frac{D_{ab} \cdot Re^{\frac{3}{4}} \cdot Sc^{\frac{2}{3}}}{5.7 \cdot v}$$

[redacted]

Next, we solve for the characteristic mass transfer time scale with new k_c and L_b....

$$\tau_{mt} := \frac{L_b}{k_c}$$

[redacted]

Finally, we solve for the Damkohler number.....

$$D_A := \frac{\tau_{mt}}{\tau_{rxn}}$$

[redacted]

This Damkohler number is less than 10, so we would use Model #2 to model the system because mass transfer has little effect on the system and can be approximated using the reaction-limited case.

Appendix I – Tanks-In-Series Calculations

Tanks-in-series solution from Clark (1996) for 1 Tank

$N := 1$ $h_{sys} := .4572m$ $l_{sys} := 1m$ $w_{sys} := 1m$ $Q := 1.026 \cdot 10^{-3} \frac{L}{sec}$ $n := .5$

$k_{PCE} := 8.292 \cdot 10^{-5} sec^{-1}$ $M_{bio} := 40.66mg$ $V_{sys} := h_{sys} \cdot l_{sys} \cdot w_{sys} \cdot n$ $V_{sys} = 2.286 \times 10^{2} L$

$X_{bio} := \frac{M_{bio}}{V_{sys}}$ $X_{bio} = 1.779 \times 10^{-1} \frac{mg}{L}$ $K_{sPCE} := .0896 \frac{mg}{L}$ $C_{in} := .0005 \frac{mg}{L}$

$k_{first} := \frac{k_{PCE} \cdot X_{bio}}{K_{sPCE}}$ $k_{first} = 1.646 \times 10^{-4} sec^{-1}$ $t_{bar} := \frac{V_{sys}}{Q}$ $t_{bar} = 2.228 \times 10^{5} sec$

$$C_{out} := C_{in} \cdot \left[\frac{1}{\left(1 + \frac{k_{first} \cdot t_{bar}}{N} \right)^{N}} \right]$$

[redacted]

Tanks-in-series solution from Clark (1996) for 18 Tanks

$N := 18$ $h_{sys} := .4572m$ $l_{sys} := 1m$ $w_{sys} := 1m$ $Q := 1.026 \cdot 10^{-3} \frac{L}{sec}$ $n := .5$

$k_{PCE} := 8.292 \cdot 10^{-5} sec^{-1}$ $M_{bio} := 40.66mg$ $V_{sys} := h_{sys} \cdot l_{sys} \cdot w_{sys} \cdot n$ $V_{sys} = 2.286 \times 10^{2} L$

$X_{bio} := \frac{M_{bio}}{V_{sys}}$ $X_{bio} = 1.779 \times 10^{-1} \frac{mg}{L}$ $K_{sPCE} := .0896 \frac{mg}{L}$ $C_{in} := .0005 \frac{mg}{L}$

$k_{first} := \frac{k_{PCE} \cdot X_{bio}}{K_{sPCE}}$ $k_{first} = 1.646 \times 10^{-4} sec^{-1}$ $t_{bar} := \frac{V_{sys}}{Q}$ $t_{bar} = 2.228 \times 10^{5} sec$

$$C_{out} := C_{in} \cdot \left[\frac{1}{\left(1 + \frac{k_{first} \cdot t_{bar}}{N} \right)^{N}} \right]$$

[redacted]

Bibliography

Agency for Toxic Substances and Disease Registry (ATSDR). n. pag. http://www.atsdr.cdc.gov. 29 July 2001.

Anderson, James E. and Perry L. McCarty. "Model for Treatment of Trichloroethylene by Methanotrophic Biofilms," *Journal of Environmental Engineering*, 120(2): 379-400 (1994).

Armenante, Piero M. "Bioreactors," in *Biotreatment of Industrial and Hazardous Waste.* Ed. Morris Levin. New York: McGraw-Hill, Inc., 1993.

Bagley, D. M., J. M. Gossett. "Tetrachloroethene Transformation to Trichloroethene and cis-1,2-Dichloroethene by Sulfate-Reducing Enrichment Culture," *Applied and Environmental Microbiology*, 56(8): 2511-2516 (1989).

Bleckmann, Charles A., Edward C. Heyse, and Mark N. Goltz. "Natural Remediation Processes," in *Natural Remediation of Environmental Contaminants: Its Role in Ecological Risk Assessment and Risk Management*. Ed. Michael Swindoll. Pensacola FL: Society of Environmental Toxicology and Chemistry, 2000.

Characklis, William G. and Kevin C. Marshall. *Biofilms.* New York: Wiley, 1990.

Charbeneau, Randall J. *Groundwater Hydraulics and Pollutant Transport*. Upper Saddle River NJ: Prentice-Hall, Inc., 2000.

Clark, Mark M. *Transport Modeling for Environmental Engineers and Scientists.* New York: John Wiley & Sons, Inc., 1996.

Dykaar, Bruce B. and Peter K. Kitanidis. "Macrotransport of a Biologically Reacting Solute Through Porous Media," *Water Resources Research*, 32(2): 307-320 (1996).

Fennell, Donna E. and James M. Gossett. "Modeling the Production of and Competition for Hydrogen in a Dechlorinating Culture," *Environmental Science and Technology*, 32(16): 2450-2460 (1998).

Forrester, Jay W. and Peter M. Senge. "Tests for Building Confidence in System Dynamics Models," *TIMS Studies in the Management Sciences*, 14: 209-228 (1980).

Headley, John V., Juergen Gandrass, Juergen Kuballa, Kerry M. Peru, and Yiling Gong. "Rates of Sorption and Partitioning of Contaminants in River Biofilm," *Environmental Science and Technology*, 32(24): 3968-3973 (1998).

Hoefar, Colby D. *Modeling Chlorinated Ethene Removal in Constructed Wetlands: A System Dynamics Approach*. MS Thesis, AFIT/GEE/ENV/00M-09. School of Engineering, Air Force Institute of Technology (AU), Wright-Patterson AFB OH, 2000.

Jones, Steven M., Daniel W. Smith, and Alan F. Weston. "Natural Remediation in Wetlands," in *Natural Remediation of Environmental Contaminants: Its Role in Ecological Risk Assessment and Risk Management*. Ed. Michael Swindoll. Pensacola FL: Society of Environmental Toxicology and Chemistry, 2000.

Lee, M. D., J. M. Odom, and R. J. Buchanan Jr. "New Perspectives on Microbial Dehalogenation of Chlorinated Solvents: Insights from the Field," *Annual Reviews Microbiology*, 52: 423-452 (1998).

Lorah, Michele M. and Lisa D. Olsen. "Natural Attenuation of Chlorinated Volatile Organic Compounds in a Freshwater Tidal Wetland: Field Evidence of Anaerobic Degradation," *Water Resources Research*, 35(12): 3811-3827 (1999).

MacDonald, Thomas R., Peter K. Kitanidis, Perry L. McCarty, and Paul V. Roberts. "Mass-Transfer Limitations for Macroscale Bioremediation Modeling and Implications on Aquifer Clogging," *Ground Water*, 37(4): 523-531 (1999).

Maier, Raina M., Ian L. Pepper, and Charles P. Gerba. *Environmental Microbiology*. San Diego: Academic Press, 2000.

Marshall, Kevin C. "Colonization, Adhesion, and Biofilms," in *Manual of Environmental Microbiology*. Ed. Christon J. Hurst. Washington DC: ASM Press, 1997.

Maymo-Gatell, X., V. Tandoi, J. M. Gossett, and S. H. Zinder. "Characterization of an H_2-Utilizing Enrichment Culture that Reductively Dechlorinates Tetrachloroethene to Vinyl Chloride and Ethene in the Absence of Methanogenesis and Acetogenesis," *Applied and Environmental Microbiology*, 61(11): 3928-3933 (1995).

McCarty, Perry L. "Biotic and Abiotic Transformations of Chlorinated Solvents in Ground Water," *Symposium on Natural Attenuation of Chlorinated Organic in Ground Water, Dallas, TX*. EPA/540/R-96/509. Washington DC: USEPA Office (1996).

McCarty, Perry L. "Breathing with Chlorinated solvents," *Science*, 276: 1521-1522 (1997).

National Research Council. *Groundwater and Site Cleanup: Improving Management of Persistent Contaminants.* Washington DC: National Academy Press, 1999.

Polprasert, C., N. R. Khatiwada, and J. Bhurtel. "Design Model for COD Removal in Constructed Wetlands Based on Biofilm Activity," *Journal of Environmental Engineering*, 124(9): 838-843 (1998).

Rittmann, Bruce E. "The Significance of Biofilms in Porous Media," *Water Resources Research*, 29(7): 2195-2202 (1993).

Rittmann, Bruce E. and Perry L. McCarty. "Model of Steady-State-Biofilm Kinetics," *Biotechnology and Bioengineering*, 22: 2343-2357 (1980).

Rittmann, Bruce E. and Perry L. McCarty. "Substrate Flux into Biofilms of any Thickness," *Journal of the Environmental Engineering Division*, 107(EE4): 831-847 (1981).

Rittmann, Bruce E. and Perry L. McCarty. "Variable-Order Model of Bacterial-Film Kinetics," *Journal of the Environmental Engineering Division*, 104(EE5): 889-900 (1978).

Roberts, Randall L. *Modeling Chlorinated Ethene Removal in the Methanogenic Zone of Constructed Wetlands: A System Dynamics Approach.* MS thesis, AFIT/GEE/ENV/01M-17. School of Engineering, Air Force Institute of Technology (AU), Wright-Patterson AFB OH, 2001.

Sáez, Pablo B. and Bruce E. Rittmann. "Improved Pseudoanalytical Solution for Steady-State Biofilm Kinetics," *Biotechnology and Bioengineering*, 32: 379-385 (1988).

Sayles, Gregory D. and Makram T. Suidan. "Biological Treatment of Industrial and Hazardous Wastewater," in *Biotreatment of Industrial and Hazardous Waste.* Ed. Morris Levin. New York: McGraw-Hill, Inc., 1993.

Schwarzenbach, René P., Philip M. Gschwend, and Dieter M. Imboden. *Environmental Organic Chemistry.* New York: John Wiley & Sons, Inc., 1993.

Suidan, Makram T. and Yi-Tin Wang. "Unified Analysis of Biofilm Kineitcs," *Journal of Environmental Engineering*, 111(5): 634-646 (1985).

Vogel, Timothy M. and Perry L. McCarty. "Abiotic and Biotic Transformations of 1, 1, 1-Trichloroethene Under Methanogenic Conditions," *Environmental Science and Technology*, 21(12): 1208-1213 (1987).

Wang, Yi-Tin, Makram T. Suidan, and Bruce E. Rittmann. "Kinetics of Methanogens in an Expanded-Bed Reactor," *Journal of Environmental Engineering*, 112(1): 155-170 (1986).

Wiedemeier, Todd H., Hanadi S. Rifai, Charles J. Newell, and John T. Wilson. *Natural Attenuation of Fuels and Chlorinated Solvents in the Subsurface*. New York: John Wiley & Sons, Inc., 1999.

Williamson, Kenneth and Perry L. McCarty. "A Model of Substrate Utilization by Bacterial Films," *Journal of the Water Pollution Control Federation*, 48(1): 9-24 (1976).

Vita

Captain Jason S. Campbell was born in Flemington, New Jersey. He graduated from Satellite High School in Satellite Beach, Florida in 1992. In 1993, he attended the United States Air Force Academy Preparatory School in Colorado Springs, Colorado and earned an appointment to the United States Air Force Academy. He graduated with an undergraduate degree in Civil Engineering in May 1997 and received a reserve commission in the Air Force.

His first assignment was to the 42nd Civil Engineer Squadron at Maxwell AFB, Alabama where he served as the Military Construction Project Manager and Squadron Executive Officer. While stationed at Maxwell, he deployed to Eskan Village (Riyadh), Kingdom of Saudi Arabia and served as the Chief of Combat and Maintenance Engineering for the 4409th Civil Engineering Squadron. In August of 2000 he entered the Graduate Engineering and Environmental Management program, School of Engineering, Air Force Institute of Technology. Upon graduation, he will be assigned to Andersen AFB, Guam as a base-level civil engineer.

REPORT DOCUMENTATION PAGE	Form Approved OMB No. 074-0188

1. REPORT DATE *(DD-MM-YYYY)*	2. REPORT TYPE	3. DATES COVERED *(From – To)*
26-03-2002	**Master's Thesis**	Sep 2000 – Mar 2002

4. TITLE AND SUBTITLE

A COMPARISON OF MODELING APPROACHES IN SIMULATING CHLORINATED ETHENE REMOVAL IN A CONSTRUCTED WETLAND BY A MICROBIAL CONSORTIA

5a. CONTRACT NUMBER

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)

Campbell, Jason S., Captain, USAF

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAMES(S) AND ADDRESS(S)

Air Force Institute of Technology
Graduate School of Engineering and Management (AFIT/EN)
2950 P Street, Building 640
WPAFB OH 45433-7765

8. PERFORMING ORGANIZATION REPORT NUMBER

AFIT/GEE/ENV/02M-02

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

AFRL/MLQ
Dr Tom Stauffer
Barnes Ave
Tyndall AFB FL 32403
(850) 283-6059

10. SPONSOR/MONITOR'S ACRONYM(S)

11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT

APPROVED FOR PUBLIC RELEASE; DISTRIBUTION UNLIMITED.

13. SUPPLEMENTARY NOTES

14. ABSTRACT

The purpose of this study is to compare different approaches to modeling the reductive dechlorination of chlorinated ethenes in the anaerobic region of an upward flow constructed wetland by microbial consortia. A controlled simulation experiment that compares three different approaches to modeling the degradation of chlorinated ethenes in wetland environments is conducted and investigates how each of the modeling approaches affect simulation results. Concepts like microbial growth in the form of a biofilm and spatially varying contaminant concentrations bring the validity of the CSTR assumption into question. These concepts are incorporated into the different modeling approaches to evaluate the CSTR assumption. Model simulations show that spatially varying contaminant concentrations have a significant effect on contaminant effluent concentrations. Additionally, the significance of the incorporation of a biofilm concept depends on the time characteristics of both diffusive mass transport and reaction kinetics.

15. SUBJECT TERMS

Constructed Wetland, Perchloroethene, PCE, Trichloroethene, TCE, Bioremediation, Biodegradation, Chlorinated Groundwater Contaminants, Vinyl Chloride, Dichloroethene, Anaerobic Degradation, Biofilm

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			Michael L. Shelley (ENV)
U	U	U	UU	112	19b. TELEPHONE NUMBER *(Include area code)* (937) 255-3636, ext 4594; e-mail: Michael.Shelley@afit.edu